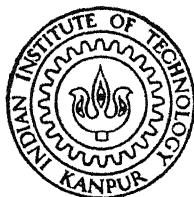


ELECTROPHORETIC DEPOSITION OF β -ALUMINA AND MAGNESIA

By

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DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
AUGUST, 1978

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ELECTROPHORETIC DEPOSITION OF B—ALUMINA AND MAGNESIA

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

By
D. U. KRISHNA RAO

ESAP 1

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DEPARTMENT OF METALLURGICAL ENGINEERING
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CERTIFICATE

Certified that this work on "Electrophoretic Deposition of β -Alumina and Magnesia" by D.U. Krishna Rao has been carried out under my supervision and that this has not been submitted elsewhere for a degree.



(E.C. Subbarao)

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ABSTRACT

Electrophoretic deposition is fast becoming an important process for coating purposes and the fabrication of ceramic shapes since it is simple and inexpensive. The purpose of the present work is basically to evaluate various parameters which affect electrophoretic deposition such as, vehicles used for preparing suspensions, the role of grinding, additives, the voltage and duration of deposition, electrode separation etc. These parameters have been studied, wherever possible in a quantitative way, with particular reference to three important ceramic oxides namely, β -alumina, magnesia and alumina.

PART A: Electrophoretic Deposition of β -alumina:

β -alumina is a solid electrolyte used in sodium-sulphur battery. Among the vehicles investigated viz., benzyl alcohol, dichloromethane and five different varieties of amyl alcohol for the electrophoretic deposition of β -alumina, amyl alcohol (BDH) was found to give satisfactory deposits without bubbling even at 1000 V. With concentration of the suspension, the specific yield increased drastically above 60 g/100 cc suspension and the conductivity decreased. First 1-2 hrs of grinding was found to increase the specific yield and conductivity in a more drastic way than further grinding. The specific yield was found to increase linearly with voltage and time of deposition, thereby verifying the

relevant kinetic equations. With temperature, the specific yield increased linearly with an accompanying increase in conductivity of the suspension. Addition of a few drops of ethylene glycol mono-ethylene ether was found to increase the yield by 8 times. The equation relating the specific yield to the electrode separation has been verified. But a limitation of this equation was detected when the electrode separation becomes very small.

PART B.I: Electrophoretic Deposition of Magnesia:

Amyl alcohol was found to be a better medium than benzyl alcohol and dichloromethane for electrophoretic deposition of magnesia. An abnormal increase in specific yield rate was observed at concentrations greater than 20 g/100 cc and is attributed to drag forces. Grinding (upto 8.5 hrs) had no effect on specific yield. On the other hand, specific yield increases in a predictable manner as the distance between the two electrodes is decreased, or voltage or time of deposition is increased.

PART B.II: Electrophoretic Deposition of Alumina:

Amyl alcohol and benzyl alcohol were found to be satisfactory vehicles for the deposition of alumina. For a given type of vehicle, the lower conductivity vehicle gives good yields. The specific yield increased linearly with applied voltage and duration of deposition. Grinding of the magnesia suspension does not alter specific yield significantly.

I. INTRODUCTION

The work described here is mainly on electrophoretic deposition. The phenomenon of "Electrophoresis" was first discovered by F.F. Ruess in the year 1809. Electrophoresis is an electrokinetic phenomenon in which charged particles are moved and deposited under the influence of an electric field.

I.1 Applications:

Electrophoresis has become an important tool in biochemistry, physiology and medicine. This technique is widely used in rubber and paint industry.⁽¹⁾ In the preserves industry the tin cans used are enamelled on the inside by the electrophoresis process.⁽²⁾ Corrosion resistant coatings on metallic substrates are achieved by this versatile technique. They are: Aluminide coatings from aqueous and nonaqueous vehicles on gas turbine blades, nickel- and cobalt-base superalloys.⁽³⁾ Shyne et al.⁽⁴⁾ discussed the deposition of nickel, nickel-chromium, and nickel-chromium-iron coatings onto base metals using alcohol as vehicle. Lamb and Reed⁽⁵⁾ deposited aluminum, silicon, germanium, GeO_2 , WO_3 , NiO and BaTiO_3 from organic liquids. Gutierrez et al.⁽⁶⁾ and Ortner⁽⁷⁾ used isopropanol and nitromethane to deposit refractory metals, oxides and carbides. Corrosion and heat resistant oxide coatings MgO ^(8,9) and Al_2O_3 ⁽¹⁰⁾ from alcohol suspensions are given on metallic substrates. Choudhary⁽¹¹⁾ could deposit TiO_2 , NiO , Cr_2O_3

and Al_2O_3 from aqueous suspensions. $\text{BaSr}(\text{CO}_3)_2$ coating in radio valves and an insulating Al_2O_3 coating on filaments⁽¹²⁾ are well achieved by electrophoresis. The British Iron and Steel Institute⁽¹³⁾ described continuous aluminum coating of steel strip.

Producing ceramic bodies by electrophoresis is of much more recent origin. Alumina ogives were produced by Andrews et al.⁽¹⁴⁾ and zirconia tubes by Lazennec and Fally⁽¹⁵⁾. Especially noteworthy is the active research on β -alumina depositions. β -alumina tubes were prepared by Lazennec et al.^(15,16), Kennedy et al.⁽¹⁷⁾ and Powers⁽¹⁸⁾. An attempt was made by Baral⁽¹⁹⁾ in this laboratory.

I.2 Advantages:

I.2.1 As a coating technique: Coatings can be given by dipping, painting, spraying, or by electrophoresis. Among these methods, electrophoretic deposition has particular advantages. This method provides superior coverage to relatively inaccessible surfaces of the part being coated, better uniformity at edges, and reduced losses from over-spray and drag-out normally associated with spraying and dipping. Electroplating and electrophoresis processes seems to be alike, but, there are several key points of difference between the two processes. For example, whereas electroplating generally employs homogeneous solutions as the plating bath, electrophoresis can be carried out with a wide variety of conducting and non-conducting solid materials which are dispersed in a

conducting liquid medium either as an emulsion or as a macromolecular colloidal solution.

I.2.2 As a forming technique: Objects can be formed by extrusion, pressing, slip casting, or by electrophoresis. Extrusion can be used only for rods and open end tubes. In case of thin walled tubes, the percentage of rejection in the green and sintered tubes produced by pressing are more. The possible shapes which can be made by slip casting are limited in number and control over the thickness of the product is rather poor. The important advantages of forming by electrophoresis are (a) high throwing power, (b) uniform thickness of the product, (c) short deposition times required, (d) versatility, so that a wide variety of shapes are possible, and (e) relatively simple "Tooling".

I.3 Theory of Electrophoresis:

In electrophoretic deposition, the charged particles are moved and get deposited on the substrate under the influence of an electric field. The charge and its magnitude is of prime importance in electrophoresis. When phases come into contact, some redistribution of positively and negatively charged particles always takes place at the interface. This redistribution of positive and negative particles leads to the formation of an electric double layer and gives rise to an interphase potential difference. The factors affecting this electric double layer are explained in I.3.1.

I.3.1 Electric double layer: Colloidal or fine particles (1 to 20 μm) carry surface charge, which influences distribution of ions in a polar medium; ions of opposite charge (counter-ions) are attracted towards surface of the particle, and ions of like charge (co-ions) are repelled from the surface. The negative surface of the colloid attracts a surrounding layer of positive ions which may originate either from the bulk of the suspending liquid or from the surface of colloid itself. The oppositely charged ions, or 'counter-ions' are drawn to the colloid by electrostatic attraction, while thermal agitation or Brownian motion tends to distribute them uniformly throughout the solution. The charged system - the surface of the colloid and the neutralizing counter-ions is called a 'double layer'.

If the negative charge is large, some counter-ions will be so strongly attracted that they will stick to the surface of the colloid as a firmly attached compact and fixed layer, often called the Stern layer. This layer partially neutralizes the charge and electrostatic attraction of the colloid so that the remaining counter-ions can, on the average, be farther away, while still being kept in the immediate vicinity of the colloid. They form the diffuse part of the double layer generally referred to as Gouy layer. Negative ions of any salt present tend to be repelled from the immediate vicinity of the colloid particles. The thickness of the diffuse double layer decreases to a few angstroms with higher concentrations of salt.

The attached ions are held by electrostatic and physical forces which differ for each ion; i.e., each ion possesses a specific adsorption potential. The potential drop in the liquid phase in contact with the colloidal particle is made up of two parts: (1) the potential in the diffuse part of the double layer - the Gouy, electrokinetic or zeta potential; and (2) the potential in the fixed portion of the double layer - the Stern potential.

The zeta potential is a measure of the charge of the diffuse double layer and of its extent away from the surface. This potential is, therefore, related to the force and distance over which particles can repel each other and thus prevent flocculation of dispersions. The zeta potential (ξ) is expressed by the relation,

$$\xi = 4\pi\eta/\mu (9 \times 10^4/\epsilon) \quad (\text{I.1})$$

where η is the viscosity of the medium, μ is the mobility of the particles and ϵ is the dielectric constant of the medium.

Some workers have assigned a critical value for zeta potential - a value of more than about 25 mV may result in stable dispersions. The addition of electrolytes generally compresses the double layer thickness and lowers the zeta potential.⁽²⁰⁾

I.3.2 Mode of charging: In the case of a finely divided solid phase dispersed in a liquid, the mechanisms⁽²¹⁾ of charging of the particles is explained as follows. One mechanism involves unequal transfer of positive and negative ions from the surface of

surface of the solid phase into the liquid. As a result the solid phase acquires a certain charge relative to the liquid, an electric double layer is formed and an interphase potential difference arises, preventing further transfer of charged particles from one phase into the other.

The second mechanism involves preferential adsorption of one type of ion on the solid phase, giving rise to an electric double layer at the particle surfaces and to an interphase potential difference.

The third mechanism is associated with orientation of dipolar molecules present on the surface of the solid phase; these dipoles then induce orientation of neighbouring molecules both in the liquid and in the solid phase and form an electric double layer. This mechanism of double layer formation does not operate in ceramic masses⁽⁸⁾, but the first two are always present simultaneously. This is because, in practice, the liquid always contains a certain amount of foreign ions which can be adsorbed on the solid phase, and because ions always migrate, even if in very small quantities, from the solid phase surface into the liquid.

The second mechanism is the one of most interest in relation to deposition, as it is possible to vary the magnitude and sign of the charge conferred onto the solid particles by addition of small amounts of different electrolytes to the liquid. It is therefore possible to regulate the properties of the resultant suspensions.

I.3.3 Conditions for good electrophoretic deposition: Two different theories of electro-deposition have been advanced. In the first^(9,22) a cumulative influence is considered of several layers of particles pressing upon each other, causing the particles close to the electrode to adhere to it and to each other. The second theory presented regards flocculation by electrolyte to be the final cause of deposit formation.

The local increase in electrolyte concentration near the electrodes lowers the local field by a factor which may easily amount to 10 or more. This would make the accumulation mechanism still less probable. It is, however, conceivable that in other systems the products of the electrode reaction are weakly ionized if at all. In such cases a decrease of the local electrolyte concentration would follow, coupled with an increase in the local field, and the flocculation mechanism would thus be ruled out in favour of the accumulation mechanism.

I.3.3.1 Stability of suspension: For the particles to be deposited, the suspension must be stable in bulk and should be unstable in the neighbourhood of the electrode.⁽²³⁾ The particles travel to the electrode in the electric field independently of one another just as they do when settling from a suspension under the influence of gravity. If the suspension remained stable right upto the electrode, a compact viscous layer would form but with no internal cohesion, and such a layer would 'drip' from the electrode. To give good electrophoretic deposition, the particles must coagulate

at the electrode.⁽²⁴⁾ For this purpose a suspension is used that is only just stable, and the process is arranged in such a way that electrolysis products formed by the passage of current through the electrode surface will cause flocculation at that surface. In arriving at conditions of optimum dispersion and stability, use was made of the concept of minimum apparent viscosity.⁽²⁵⁾

I.3.3.2 Role of ζ and ϵ : There is a critical distance between the particles in the suspension to form the deposit.⁽²²⁾ Evidently, the smaller the critical distance the more regular will be the structure of the deposit and the greater its mechanical stability. The critical distance, in turn, depends on the repulsive and attractive forces between the particles, the former being undoubtedly due to the electric charges. So, high zeta potential is especially favourable for electrophoretic deposition. But, in case of β -alumina, the best electrophoretic deposits occurred when the zeta potential had a low absolute value.⁽²⁶⁾ High dielectric constant of the medium generally goes with a strong electrolytic dissociative power

and therefore with a well developed electrical double layer. But in case of electrophoresis of β -alumina, good deposits were obtained with organic media having dielectric constant in the range 12-25 only.⁽¹⁸⁾

I.3.3.3 Critical time: During electrophoresis, the particles are accumulated at the electrode, but the deposit stays fluid as long as the double-layer repulsion between the particles prevents actual

contact. At the critical time t^* practically the whole deposit turns rigid within a few seconds. Below t^* no adherent deposit is found. An important factor in explaining why at $t = t^*$ practically the layer turns rigid in a few seconds may be the following.⁽²⁷⁾

When as a result of the flocculation mechanism the particles in the electrode area touch, part of the medium is squeezed, thereby bringing the electrolyte concentration in the adjacent layer, which is already high, on the flocculation value. Owing to convection this mechanism might fail at the circumference of the layer, which explains why at $t > t^*$ still a small part of the layer flows off.

The following simple equation gives the relation between the critical time and the conditions of electrodeposition⁽²⁸⁾:

$$t^* = q V^{-2} \kappa^{-2} \quad (I.2)$$

Here, q is a constant which depends only on the geometry of the electrodes and the properties of the suspension, V is the voltage applied and κ the specific conductivity of the suspension.

Thus, the critical time decreases with voltage and specific conductivity of the suspension. Its variation with concentration of the suspension was observed to be erratic.⁽²⁷⁾

I.4 Kinetics of Electrophoretic Deposition:

The electrophoretic yield is found to follow an extremely simple and straightforward law⁽⁹⁾, being proportional to the time (t), the concentration (c), the area which is being coated (S) and

the electric field perpendicular to the surface $S(dV/dn)$. This is expressed by

$$Y = \bar{\sigma} \cdot c \cdot \int \left\{ dV/dn \cdot dS \cdot dt \right. \quad (I.3)$$

σ is a constant which depends on the chemical composition of the suspensions but not on the physical conditions of the experiments. The constant σ represents a lower limit for the electrophoretic velocity of the particles and is equal to the electrophoretic velocity when every particle reaching the coating electrode actually partakes in the formation of a deposit; on the other hand, if only a fraction of the particles is deposited, σ will be less.

In terms of the cell dimensions and physical constants of the suspension, Avgustinik et al.⁽⁸⁾ derived a similar equation to find the electrophoretic yield, γ_t . This is expressed by

$$\gamma_t = \frac{U \epsilon \cdot c \cdot l}{3 \ln \frac{r_1}{r_2} \eta} \quad (I.4)$$

where U is the applied voltage, l the length of the coating electrode dipped in the suspension, r_1 , r_2 are the radii of the inner and outer electrodes respectively, and η the viscosity of the vehicle. The other symbols have the usual meaning.

The amount deposited, A can be expressed in terms of the current I and the specific conductivity γ of the suspension as follows⁽¹²⁾:

$$A = \frac{I \cdot c \cdot l \cdot \epsilon}{\gamma \cdot 4 \pi \eta} \quad (I.5)$$

The other symbols have the usual meaning.

From these equations (I.3, I.4 and I.5), it is clear that the yield increases linearly with applied voltage, time of deposition, concentration of suspension, area of the dipped electrode and with lowering the conductivity of the suspension and viscosity of the vehicle. The yield increases as the electrode separation decreases. The restrictions on ϵ and ϵ_1 are explained in the Section I.3.3.2.

I.4.1 Concentration: A suspension has a higher viscosity than the suspending liquid. In dilute suspensions the effect is relatively small and may be considered simply a consequence of an increased velocity gradient $\frac{dv}{dx}$ between particles in the liquid, as contrasted to the average dv/dx through the bulk of the suspension. Thus,

$$\eta_b/\eta_l = (dv/dx)/(dv/dx)_{ave} \quad (I.6)$$

where η is the viscosity coefficient, and the subscripts, b, l and ave, refer to bulk, liquid, and average, respectively. (29)

In more concentrated suspensions, there is mutual interference of the suspended particles, so that the bulk viscosity increases quite rapidly. Michaels⁽³⁰⁾ gives the empirical relationship in terms of the volume fraction of the solids present C.

$$\eta_b/\eta_l = 1 + [1.25 C / (1 - C/0.74)]^2 \quad (I.7)$$

This indicates a rapid increase in viscosity as the solid content is increased in the suspension.

So, with concentration, the viscosity of the suspension increases and the viscous drag on the deposit is more.⁽¹⁸⁾ With increased concentration of the suspension, the conductivity of the suspension also changes. From equation (I.5), the yield should increase linearly with concentration, but because of the negative effects caused by the increased viscous drag and the change in conductivity of the suspension, only the overall effect is observed.

I.4.2 Temperature: The temperature of the suspension increases the conductivity of the suspension and decreases the viscosity of the medium. So, the effect of temperature on yield is the combined effect of these dependent variables.

I.4.3 Particle size: Since the forces exerted on the particles by an electric field vary in the same way as the forces acting between the particles, the formation of a deposit by electrophoresis will not be greatly influenced by the size of the particles.^(18,22,31) If the electric field is reduced, it will finally be too weak to produce a deposit at all.^(9,22) Andrews et al.⁽¹⁴⁾ noticed a slight preferential deposition of fine alumina particles. By grinding the suspension, the electrophoretic yield of β -alumina increased.^(17,18)

The process of electrification by friction the earliest known method of producing electricity, is caused by the separation of the two halves of the electrical double layer, set-up on contact between two dielectric media, when the contact is broken. The role played by friction is to increase the areas of the surface

which come into actual contact, and possibly also to change the nature of the surfaces by strain or by removal of surface films.⁽³²⁾ The generation of heat by friction, giving rise to a pyroelectric effect, may also contribute to the charge in the double layer.^(33,34) Thus, by ball milling the charge on the particles increases and thereby the yield.

I.5 Notation:

The yield defined by equations (I.3, I.4 and I.5) is expressed as weight of deposit (g). Since the yield is a function of surface area of the electrode, time and applied voltage, the data may be presented conveniently as specific yield defined as weight of deposit per unit area of the mandrel (g/cm^2) and specific yield rate defined as weight of deposit per unit area per unit time per unit voltage ($\text{g}/\text{cm}^2 \text{ min V}$).

I.6 Present Work:

The work done in this investigation is divided into two parts: Part A consists of electrophoretic deposition of beta-alumina, which is a solid electrolyte used in sodium-sulphur battery. Part B, consists of electrophoretic deposition of heat and corrosion resistant oxide coatings viz., I. Magnesia and II. Alumina.

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PART A

A. ELECTROPHORETIC DEPOSITION OF β -ALUMINA

A.I. INTRODUCTION

Progress of human civilization needs increasing amounts of energy and preferably in the form of electrical energy. Since the conventional sources of energy are getting exhausted,⁽¹⁾ one has to think about alternative sources and more economic ways of utilizing the available energy.

While research is going on for developing alternative sources of energy, the problem of storing energy cannot be overlooked. There are several ways of storing electrical energy. It can be stored in mechanical, electrical or electrochemical forms using flywheels, super conductors, water storage in reservoirs or batteries.

Let us limit our discussion to the energy sources for automotive traction. Our good old pollution-generating petroleum-burning internal combustion engine vehicles can be replaced by electric vehicles. Also petroleum is scarce and costly. In electric vehicles, secondary batteries are used. Thus, the power station energy is made "portable". Two types of vehicles may be postulated as having a wide application in the future. The general purpose electric vehicle is a near match of the general purpose internal combustion engine-powered car. A second vehicle which we shall call an urban vehicle is better suited by its lower performance and smaller size for use within urban areas.

The urban car design constraints are less severe in terms of the allowable space and weight which can be devoted to the

power source and propulsion gear. Conventional lead-acid batteries can probably provide the power and range requirements of that type of vehicle. Indeed, there have been several highly successful demonstrations of this type of vehicle.⁽²⁻⁵⁾ But, in case of general purpose vehicle, propulsion problems become much more difficult. Assuming the need for a vehicle possessing the performance, comfort and safety of today's cars, we can assign only about 30% of the vehicle's curb weight to the batteries, traction motor and control system.^(6,7)

Several reviews have assessed the candidate battery systems which could be considered for general purpose vehicle systems.^(8,9) Only higher temperature systems using fused salts or solid electrolytes are able to deliver the required power at energy densities which could make a viable electrochemical power source for general purpose automobiles.

A comparison of the characteristics of the high energy density batteries and lead-acid battery is given in Table A.1.

From this, it is clear that Na/S battery is a strong candidate as a high energy density reversible battery on the basis of low cost of active materials, size per KWh, current density and energy density.

This sodium-sulphur battery is a strong candidate not only for automotive-traction but also for load levelling in power systems to supply power at peak periods while getting charged at off-peak periods⁽¹²⁾ and electrification of rural areas coupled with intermittent sources of energy, such as solar energy etc.

TABLE A.1

Characteristics of Lead-Acid and High Energy Density Batteries (10, 11)

System	Operating temperature °C	Theoretical energy density Wh/kg	Practical energy density Wh/kg	Current density mA/cm ²	E.m.f. V	Size KWh	Life cycles	Active materials cost \$/KWh
Pb/PbO ₂	20-30	242	19.8	0.04574	10-15	1.9	20	8.50
Na/S	300-350	792	154.0	0.1524	90-100	1.7	0.03	0.50
Na/SbCl ₃	200	770	110.0	0.1220	42	2.4	0.02	2.35
LiSi/FeS ₂	400-450	946	187.0	0.2134	35-45	1.4	0.1-0.3	4.27
Zn/Cl ₂	50	462	55.0	0.04269	40-45	1.9	1.4	0.91

A.I.1 Sodium-Sulphur Battery:

Unlike the lead-acid battery, in sodium-sulphur battery sodium and sulphur in liquid form are the electrodes separated by a solid electrolyte, viz. beta-alumina ceramic. The battery operates at 300-350°C. A practical battery system (Fig. A.I.1) will have containers, seals, current collectors, auxiliary heating and insulating jackets, electrode reservoirs, etc. besides electrodes and electrolyte. However, the electrolyte is the heart of the battery and hence is emphasized here. Recent studies^(11,13) indicate that 80 percent of the cost of the battery and most of their failures may be attributed to the electrolyte.

A.I.2 Role of β -Alumina:

The chemical formula of β -alumina is $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$. This is a very good sodium ion conductor because of its peculiar crystal structure^(14,15) shown in Fig. A.I.2a and b. It has hexagonal symmetry. The crystal structure consists of Al^{3+} and O^{2-} ions in spinel-like blocks with Na^+ and O^{2-} ions loosely packed in a layer between the spinel blocks. In this $(\text{NaO})^-$ plane only some of the available sites are filled up by the sodium ions. Further, the diameter of Na^+ ion is less than the O-O distance (Fig. A.I.2b). Therefore, sodium ions can easily move from one site to another. The sodium ion conduction in this plane is maximum and in the direction normal to this $(\text{NaO})^-$ plane it is negligible. Another form of β -alumina called β'' -alumina has the

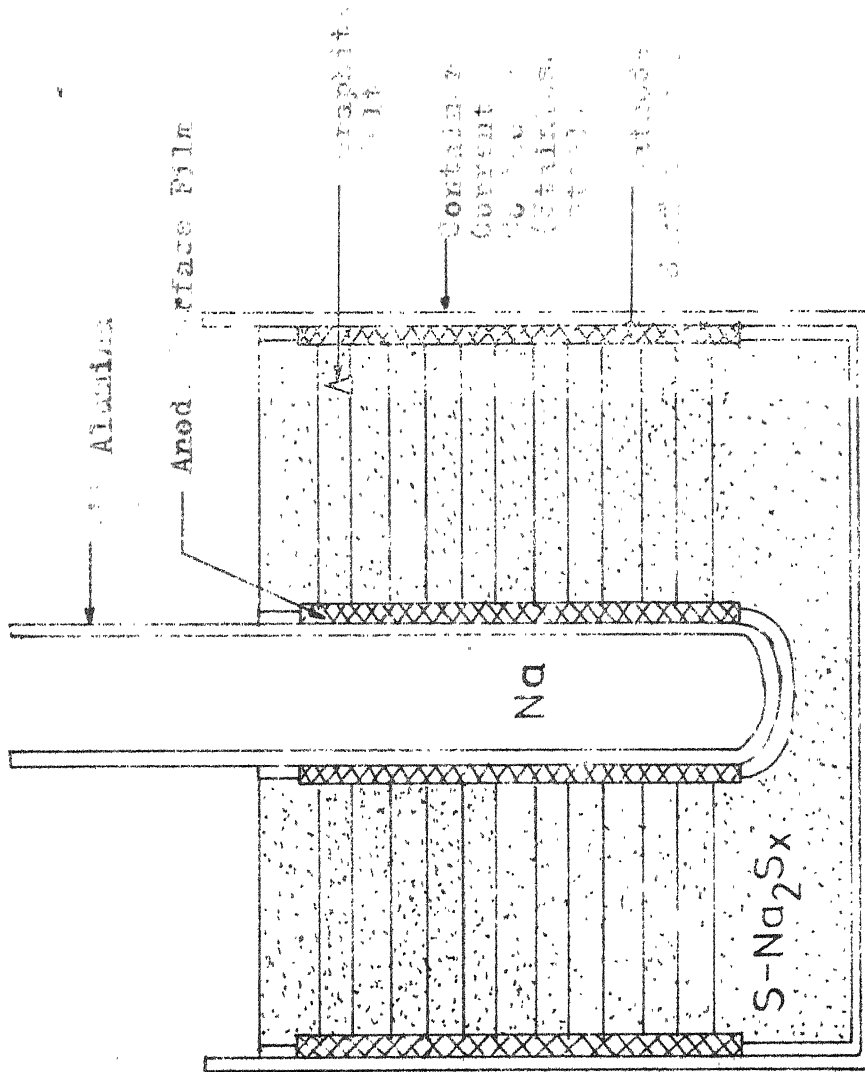


FIG. 1. A schematic diagram of a sodium-sulfur battery cell. The cell consists of a sodium electrolyte (Na) contained within a U-shaped tube. The tube is surrounded by a solid material (S-Na₂S_x). The top of the tube is connected to an anode (Aluminum) which has a surface film. The bottom of the tube is connected to a cathode (Current Collector (Stainless Steel)). The cathode is also labeled as a separator and current collector. The entire assembly is housed within a container.

Beta Alumina

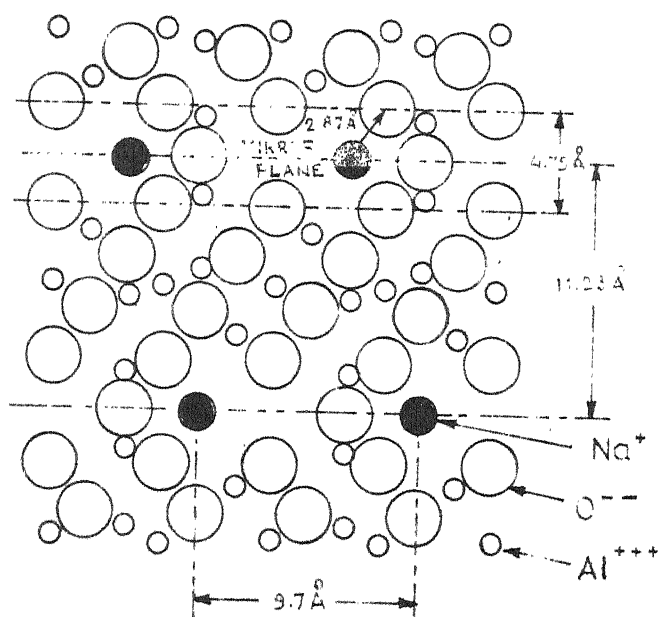


Fig. AI.2a. Arrangement of ions (110) plane of β -alumina crystal (Ref 14).

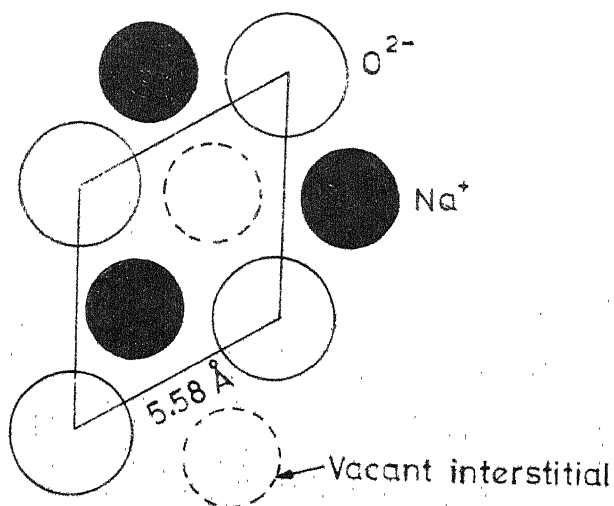


Fig. AI.2b. Arrangement of ions in the $[\text{NaO}]$ layer (Ref 14).

chemical formula $\text{Na}_2\text{O} \cdot 0.5\text{Al}_2\text{O}_3$. This is structurally similar to β -alumina with its c parameter 1.5 times that of the β form. More soda is present in β'' -alumina and therefore there are a larger number of conducting ions. Consequently, the electrical resistivity of β'' -alumina at 300°C is < 5 ohm cm and that of β -alumina is ~ 30 ohm cm, and hence β'' -alumina is preferred to β -alumina for electrolyte applications.

A.I.2.1 Shape of electrolyte ceramics: Electrolytes of different geometry were tried in Na-S batteries.⁽¹⁶⁾ They are discs, flat plates and ~~one~~ closed tubes. Because of simple geometry, discs were tried in the development of electrode structures. In case of flat plates, quite small pressure differentials across large diameter flat plate electrolytes can produce unacceptable stresses in the solid electrolyte. A large proportion of the cell volume is taken up by the seal and the cost of sealing flat plate cells escalates rapidly as the diameter is increased. These difficulties have delayed the development of the flat plate cell for commercial applications. With one end closed tubes, the sealing problems are minimised and the surface area to volume of sodium stored in this tube is more. So, tubular electrolytes in sodium-sulphur batteries are gaining in importance.

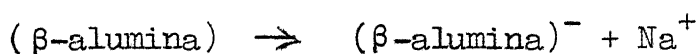
A.I.2.2 Forming of β -alumina tubes: A typical Na-S cell uses a 15 mm dia electrolyte tube 200 mm long. Slip casting,⁽¹⁷⁾ extrusion,⁽¹⁸⁾ isostatic pressing^(18,19) and electrophoresis⁽²⁰⁻²²⁾ are being explored for fabrication of these tubes, followed by

sintering, or alternately by hot pressing. The merits and demerits of these techniques are explained in Section I.2.2. The β -alumina tubes are mainly produced by isostatic pressing and by electrophoresis. The present work deals with electrophoretic deposition of β -alumina.

A.I.2.3 Present Status: Tubes of β -alumina electrolyte have been successfully fabricated by electrophoretic deposition by Powers⁽²⁰⁾, Fally et al.⁽²¹⁾ and Kennedy et al.⁽²²⁾ Fally et al.⁽²¹⁾ used polar, organic liquids such as nitromethane or trichloromethane as the vehicle for suspension. Their tubes were quite thick (200-2000 μ) and needed isostatic pressing for removal from the electrode. Kennedy et al.⁽²²⁾ used similar liquids for deposition, except that carbon electrodes were employed, so that the tubes (3-4 cm long, 0.03-0.1 mm thick) can be easily removed by burning off the carbon electrode. Powers⁽²⁰⁾ evaluated various liquids and found those alcohols to be suitable which have dielectric constants in the range of 12-25 and specific conductance of 10^{-7} to 10^{-4} (ohm cm)⁻¹. He used stainless steel electrodes and after drying the deposits, tubes came off easily from the mandrel, which had high surface finish.

A.I.2.4 Charging modes for β -alumina: There are two different charging modes for beta-alumina.^(20,22) One is the dissociation of sodium ions to give rise to a negatively charged particle.

Thus,



However, another mode is the adsorption of protons or conceivably other cations which lead to positively charged particles. Thus,



Proton donors might be water or organic acids such as benzoic or stearic acid. The charge on the particles is very much influenced by the conditions of the suspension⁽²⁰⁻²³⁾ viz., type of vehicle, moisture, acids, grinding of the suspension etc.

A.I.2.5 Parameters affecting electrophoresis: The various parameters which influence electrophoretic deposition are discussed below:

(a) Vehicle: Except with pyridine ($\epsilon = 16.3$), with all the other vehicles used in the survey experiments by Powers⁽²⁰⁾, the β -alumina particles were negatively charged. Baral⁽²⁴⁾ noticed positively charged β -alumina particles with amyl alcohol as vehicle.

(b) Moisture: Water supplies the protons and the β -alumina particles are positively charged. In case of amyl alcohol^(20,23), charge neutralization and inversion are obtained with larger additions of water, at concentrations of about 0.2 and 0.5 percent respectively. With still larger amounts of water e.g., 5 percent, charge neutralization occurs a second time and flocculation occurred.^(20,23) The critical amounts of water for charge inversions and neutralizations depends on the vehicle under consideration.^(22,23) A suspension containing water gave flaky and fluid deposit.^(20,22,23) The deposit also had a wet appearance and cracked during drying. The sources of moisture in the suspension

can be (i) the β -alumina powder which is hygroscopic, (ii) the vehicle, and (iii) absorption of moisture from atmosphere by the suspension during depositions.

(c) Grinding: The charge building on colloidal particles by grinding is explained in Section I.4.3. The role of grinding of suspension on charge and mobility of the particles depend on the type of vehicle.⁽²³⁾ In case of pentanol, the grinding decreases the mobility and after 15 hours of grinding, the charge on the particles reverses to negative. In case of nitromethane, upto $1\frac{1}{2}$ hours of grinding there was no change in mobility but further grinding increased the mobility. With dichloromethane, the negative mobility increased with just stirring. Reasonably stable dichloromethane suspensions could be obtained by stirring for 48 hours.

Three different kinds of milling (ball, vibratory and jet) were examined by Powers⁽²⁰⁾ with amyl alcohol as the dispersing liquid. Best results were obtained with ball milling. For lesser wear rates of media (balls), use was made of zirconia and 91 percent alpha-alumina balls.⁽²⁰⁾ The wear rate was less with highly concentrated suspensions (200 g/200 cc vehicle). After grinding, the suspension can be diluted to the required extent.

(d) Acids: Extensive work was done by Kennedy⁽²³⁾ on this aspect. The role of the acids and their amounts on the mobility, charge and stability of the suspension is completely dependent on the vehicles.^(23,24) Kennedy studied the effect of benzoic acid,

trichloroacetic acid on nitromethane, dichloromethane and 1-pentanol suspensions. Kennedy noticed that with the presence of acid the time of grinding to get suitable charge was minimised and also the suspension was more stable.

A.2.2.6 Outstanding problems: The following aspects were only partially studied by Powers, Fally et al., Kennedy et al. and Baral.

1. Vehicle: Powers⁽²⁰⁾ evaluated the vehicles which give satisfactory (nonfluid) deposits. Out of these good vehicles he did not study, which vehicle gives high rates of deposition.
2. Concentration: Powers⁽²⁰⁾ qualitatively stated that with higher concentrations of the suspension, viscous drag of the deposit was observed. The quantitative study of how suspension viscosity, conductivity and rate of deposition varies with concentration of the suspension was not studied.
3. Grinding: Kennedy⁽²²⁾ qualitatively stated that with grinding of the suspension, the yield increases. How the conductivity of the suspension and the yield varies was not reported.
4. Acids and additives: Their effects on yield was not studied.
5. Temperature: The effect of temperature of the suspension on yield, conductivity and viscosity of the suspension was not studied.
6. Electrode separation: The role of electrode separation on yield was not attempted.

A.I.3 Statement of the Problem:

Keeping in view of the above unsolved or partially solved problems the work of the author closely follows the work of Powers⁽²⁰⁾ and Baral⁽²⁴⁾ viz., amyl alcohol as the vehicle and steel rods as the coating electrodes. The following parameters were evaluated.

(a) Evaluation of the vehicles viz., dichloromethane, benzyl alcohol and amyl alcohol (from 5 different sources) on the basis of specific yield rates and quality of the deposit (cracks, bubbles etc.).

(b) Effect of concentration of the suspension on electrophoretic specific yield, sticking to mandrel and the conductivity of the suspension.

(c) Effect of grinding and temperature of the suspension on specific yield and conductivity of the suspension.

(d) Verification of yield equations with respect to applied voltage and time of deposition.

(e) A limited study on the addition of acids (trichloroacetic acid and ethylene glycol monoethylene ether), electrode separation on electrophoretic yield rate was also carried out.

A.II EXPERIMENTAL

A.II.1 Mixture Preparation: β "-alumina contains 1:5 moles of Na_2O and Al_2O_3 . The starting mixture prepared as follows. Alumina (Alcoa A-2) was heated to 1000°C and preserved in oven at 110°C . Sodium carbonate (BDH), which is hygroscopic was always preserved in oven at 110°C . For 100 gms mixture, 17.21 gms Na_2CO_3 and 82.788 gm Al_2O_3 were weighed using a Mettler balance to an accuracy of 0.1 mg and transferred to ball jar. 200 gms of the mixture was wet ball milled with 100 cc of acetone for 1 hr in a one litre alumina jar half filled with 1 kg sintered alumina balls of $\frac{1}{2}$ " dia. The liquid was then decanted into some beaker and air dried for 12 hrs and then kept in oven at 110°C until it was used for calcination.

A.II.2 Calcination: The oven dried mixture was transferred to platinum crucibles in lumpy form and not in powdery form as the removal of the calcine from the crucibles becomes difficult if fine powder is used. The crucibles were heated from room temperature to 1250°C in 8 hrs and calcined for 4-5 hrs at 1250°C . Then the furnace was cooled to 800°C in 2 hrs and the crucibles were taken out of the furnace and cooled to room temperature. The weight of the calcine was only 0.07 to 0.14 gms more than the calculated value for 50 gms mixture, indicating that the calcination is essentially complete. The calcine was separated from the platinum crucible using an alumina rod with a sharp end. The calcine was stored in oven at 110°C until use.

A.II.3 Characterization of Calcined Powder: 50 gms of the calcine was crushed into powdery form in an automatic pestle^{and}/mortar (The Torsion Balance Company) for half an hour. The phases in the mixture were analysed by X-ray powder diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation (cps 500, time constant 2, scan speed $2^\circ/\text{min}$ and chart speed 1 inch/min). The powder was scanned from 7° to $70^\circ 2\theta$. The calcined powder was found to consist of only β and β'' with traces of sodium aluminate. The characteristic line sets used for the phase analysis β and β'' alumina were $2\theta = 33.4^\circ$ and 34.6° or 44.8° and 46° respectively for copper radiation. A factor $f(\beta)$ was used to find the percentage of β phase in the system.

$$f(\beta) = \frac{(\text{Area under curve for } \beta \text{ line})}{(\text{Area under curve for } \beta \text{ line} + \text{Area under curve for } \beta'' \text{ line})}.$$

The $f(\beta)$ of the calcine was found to be ≈ 0.33 . Though all the materials employed in the present study were mixtures of β and β'' alumina they are referred to β -alumina hereafter for convenience.

The particle size of the calcined powder (see Fig. A.II.1) varied from 0.8 to 6μ with an average particle size of 2μ . The particle size distribution was measured using NU 2 Carlzeiss-Jena microscope. The individual particles were dispersed on a glass slide and then viewed under the microscope. The particles were dispersed on the slide as follows. A pinch of powder was taken in a test-tube and half filled with either acetone or dichloromethane which evaporates easily. Then two drops of trichloroacetic acid was added to increase the stability of the dilute suspension

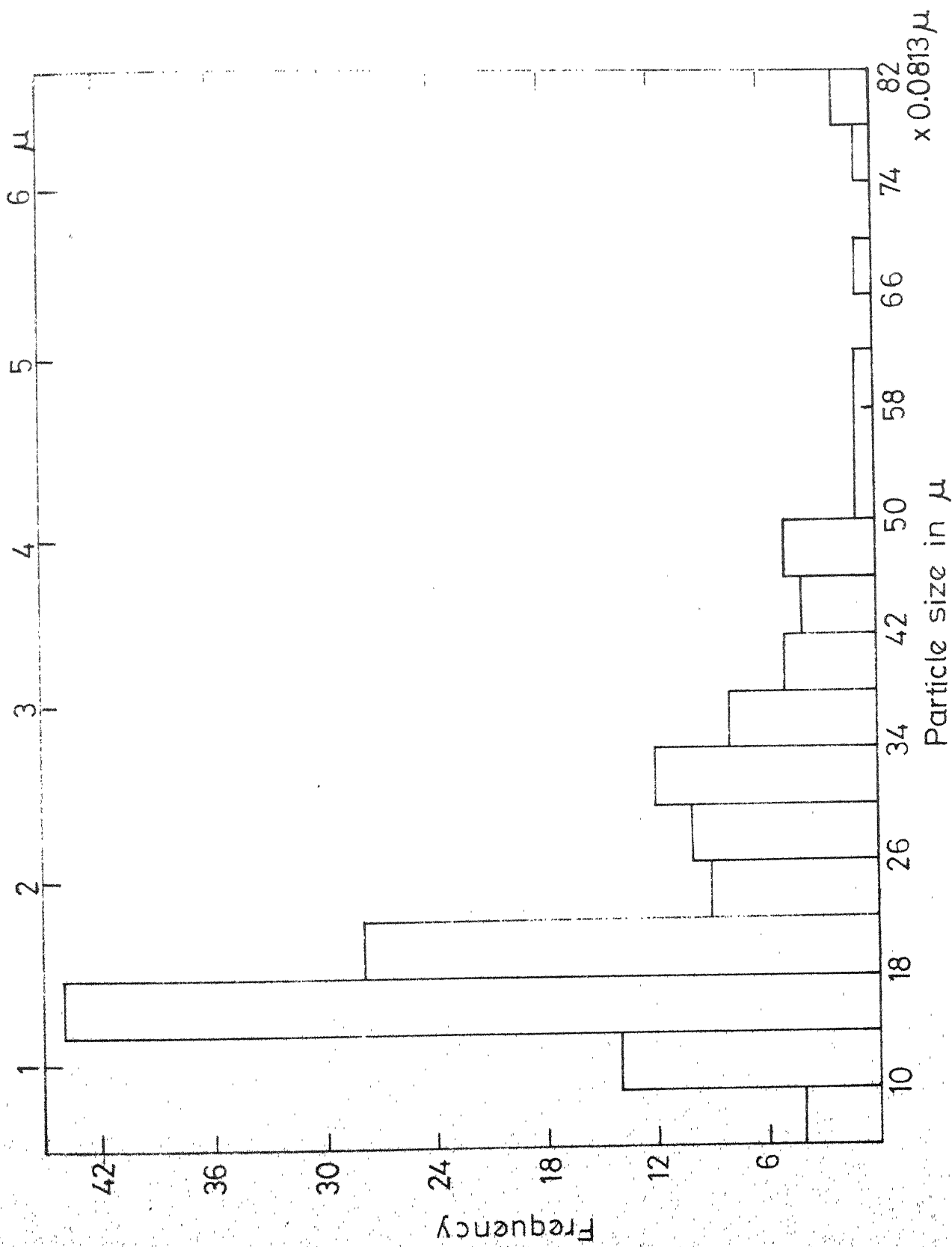


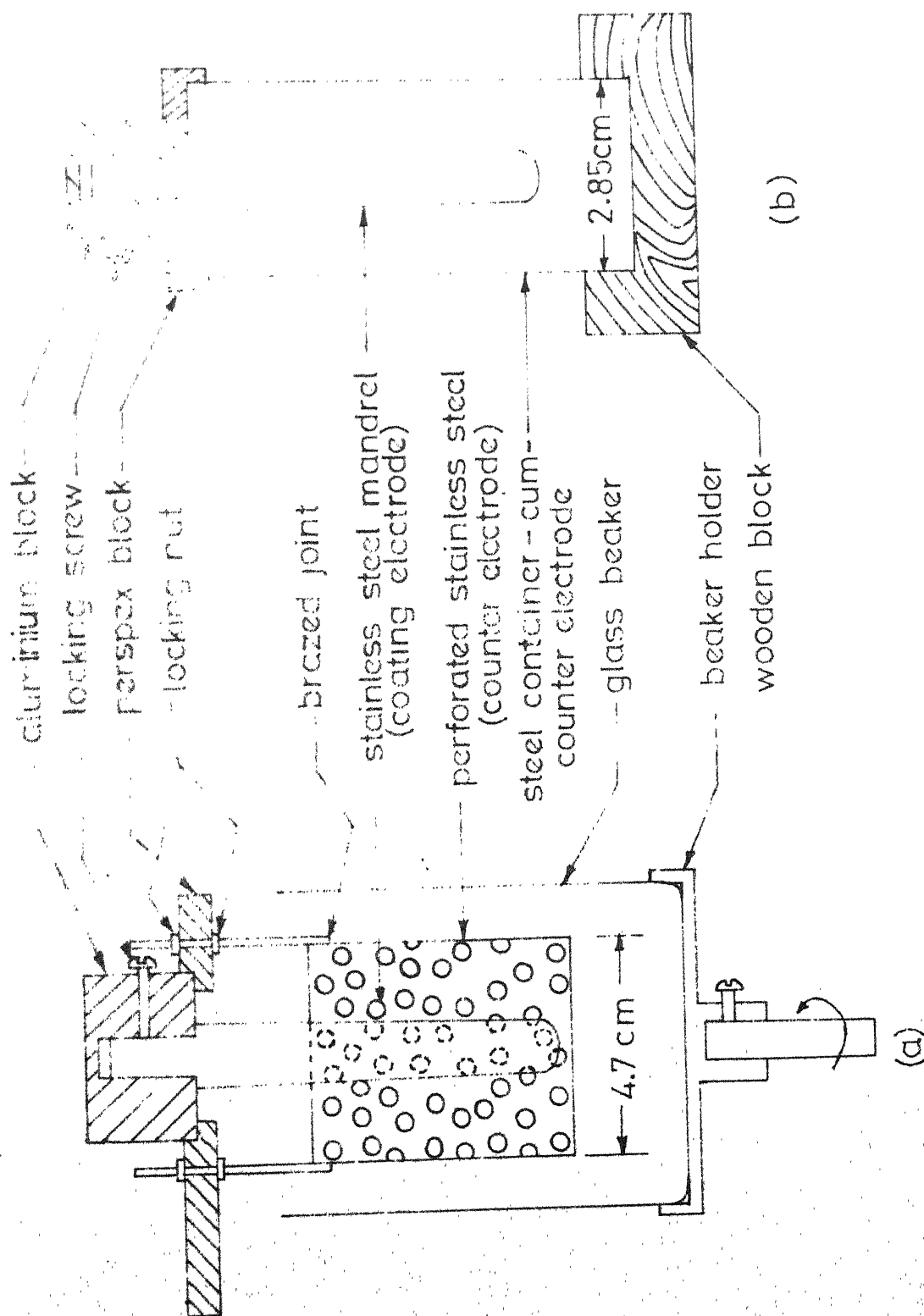
Fig.A II.1. Particle size distribution of calcined β -alumina powder.

whereby the particles do not come close to one another. Then, the test-tube with suspension was thoroughly shaken in an ultrasonic vibrator to break the agglomerates. One or two drops were dispersed on the glass slide and air dried. The back side of the slide was cleaned and the front side was viewed under microscope. About 150 particles were measured.

The powder density of the calcine was measured using a specific gravity bottle and toluene liquid. It was found to be 3.19 g/cm^3 , whereas the theoretical density of β and β'' are 3.24 and 3.27 g/cm^3 respectively.

A.II.4 Electrophoretic Cells Used: The cells used for electrophoresis are shown in Fig. A.II.2. In one case voltage was applied between the stainless steel electrodes immersed in the suspension in a glass beaker (Fig. A.II.2a). The coating electrode slightly tapered with a rounded end for easy removal of the deposit from the mandrel. The tubular counter electrode was perforated to enhance the stirring action. In order to prevent the settling of the suspension, the beaker was rotated for 1 minute before every deposition. In the second case, a one end closed tube of steel serves as the anode and as container for the suspension (Fig. A.II.2b), which was stirred before pouring into the container.

A.II.5 Electrical Circuit: The electrical connections to the electrophoresis cell are shown in Fig. A.II.3. Depending on the charge of the particles, the knob in the high voltage D.C. power



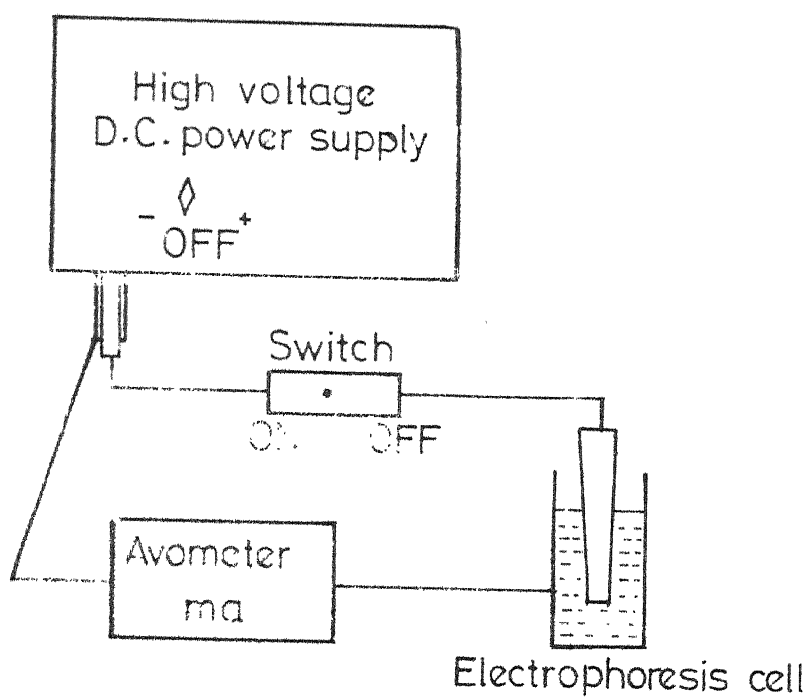


Fig. A II.3. Circuit diagram for electrophoresis.

supply (0-3000 V, Model 413 C, John Fluke Mfg. Co. Inc.) was switched to negative or positive i.e. if the particles were positively charged, the knob was switched to negative. The knob and the voltage on the power supply were adjusted first. Then, the switch was put on for electrophoretic deposition. After the deposition, the switch was put off. The current was measured using an Universal Avometer in the range 0-10 and 0-100 mA as per the requirements.

A.II.6 Suspension Preparation: Generally, 30 gms calcined powder and 50 cc liquid were taken in the ball jar and ground for $5\frac{1}{2}$ hrs then transferred into the steel can (Fig. A.II.2b). The liquid fills $\frac{1}{4}$ th volume of the can used for electrophoresis. After all the depositions were over, the remaining liquid was decanted from the can into a beaker and air dried overnight, then oven dried at 300°C for 4 hrs. The dried suspension weight was noted to compute the concentration in terms of gms of powder per 100 cc of suspension. This value was found to be more reliable than the one computed from the weight of the starting powder and the volume of the vehicle. This is so because there are some inevitable losses during grinding and transfer of the suspension from the ball jar to the electrophoretic can.

A.II.7 A Method to Find the Concentration of the Suspension: The concentration of the suspension was measured as gms of the powder per 100 cc suspension. It is computed as follows by making use of

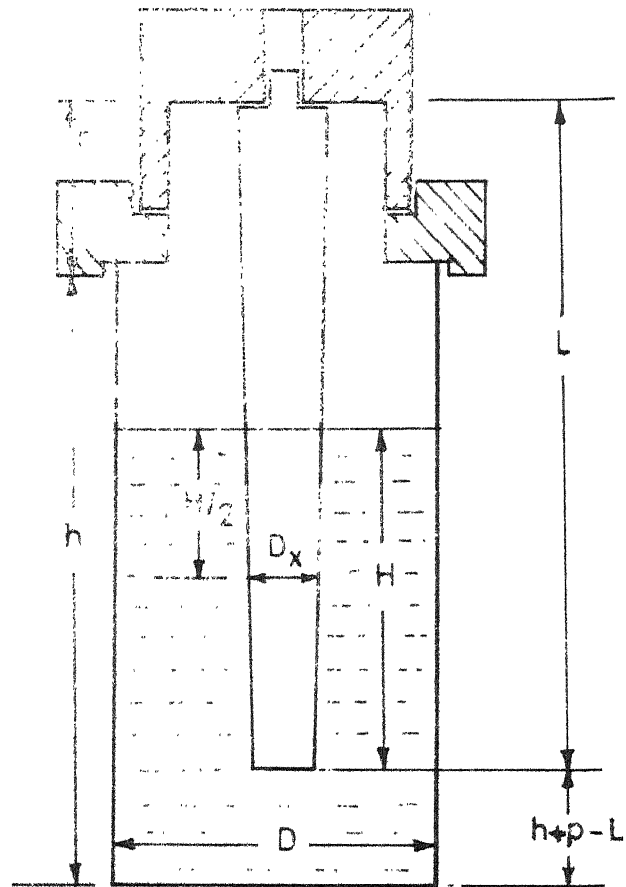


Fig.A II.4. Geometry of the cell.

the geometry of the cell. The geometry of the cell is shown in Fig. A.II.4.

H is the depth of immersion of the mandrel in the suspension and D_x is the diameter of the mandrel at half level of immersion. The distance apart between the end of the mandrel and the bottom of the can is $h + p - L$

Volume of the suspension in the can, $V =$

$$\pi \frac{D^2}{4} (H + h + p - L) - \pi \frac{D_x^2}{4} H$$

Concentration of the suspension (gms of powder/100 cc suspension)

$$= \frac{\text{amount of solid in the suspension}}{\text{volume of the suspension}} \times 100$$

The amount of solid in the suspension was calculated as follows: The amount deposited at each deposition stage was noted and after all the depositions, the remaining suspension in the can was dried and weighed. The total amount of solid in the suspension was computed by adding the weight of the dried suspension and amount deposited. Thus, the amount of solid in the suspension at any stage of deposition can be computed.

A.II.8 Specific Yield Rate Determination: The electrophoretic yield was computed by knowing the weight of the deposit, surface area of the mandrel over which the deposition has taken place, the voltage and time of deposition. The weight of the deposit and the surface area of the mandrel were measured as follows.

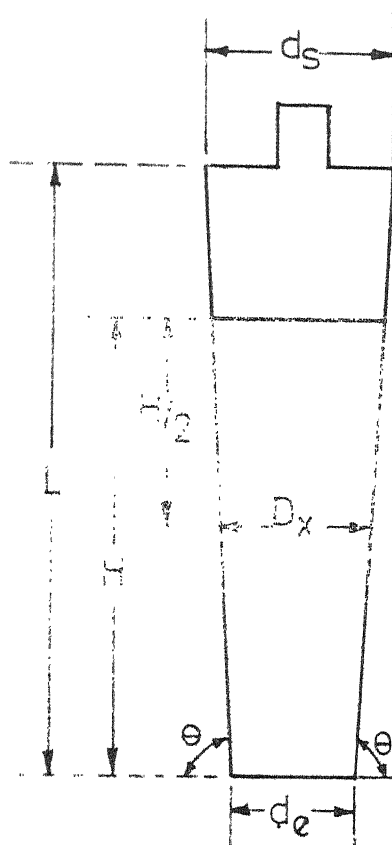


Fig.AII.5. Geometry of the mandrel.

Weight of the deposit: After air drying for 12 hrs the coated mandrel was weighed and again weighed after cleaning it. The difference between these two weights gives weight of the deposit.

Surface area of the mandrel (S): After weighing the coated mandrel the end of the deposit was cut and the length of the mandrel over which the deposition occurred was measured (H). The surface area of the mandrel over which the deposition had occurred was calculated as follows using the geometry of the mandrel (Fig. A.II.5).

$$\tan \theta = \frac{H/2}{(D_x - d_e)/2} = \frac{L}{(d_s - d_e)/2}$$

$$\frac{H}{D_x - d_e} = \frac{2L}{d_s - d_e}$$

$$\therefore D_x = \frac{(d_s - d_e)H}{2L} + d_e$$

$$S = \pi D_x H + \frac{\pi}{4} d_e^2$$

A.II.9 Conductivity of the Suspension: The conductivity of the suspension was measured using the I-V characteristics as follows:

Conductivity of the suspension =

(Current X Distance between the electrodes)/(Voltage X Surface area of the mandrel dipped in the suspension)

Only in a few cases the conductivity was estimated from the conductance measured by an impedance bridge (GR 1608) at a frequency of 1 KHz as follows:

Conductivity of the suspension =

$$\frac{(\text{Conductance} \times \text{Distance between the electrodes})}{(\text{Surface area of the mandrel dipped in the suspension})}$$

The conductivity measured by the impedance bridge is generally 6-9% more than that of the value obtained from I-V characteristics

A.III RESULTS AND DISCUSSION

A.III.1 Evaluation of Vehicles: For the electrophoresis of β -alumina dichloromethane, benzyl alcohol and amyl alcohol (from five different sources) were evaluated on the basis of electrophoretic yield rate and the quality of the deposit (Tables A.III.1 and A.III.2). The pH of the vehicles was measured with an Elico pH meter and was in the range of 5-6 and increased to 8-9 when β -alumina ($\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3$) was added, since β -alumina is basic in nature (Table A.III.1). The conductivity of the liquid and the suspension was measured with a General Radio Impedance Bridge Type 1608 at 1 KHz. On the addition of β -alumina powder, the conductivity of the liquid increased substantially except for a slight decrease in the case of dichloromethane suspension. The charge on the β -alumina particle was negative only in case of dichloromethane suspension. Dichloromethane suspension without any additives did not yield any deposit. This may perhaps be due to its low dielectric constant. Powers⁽²⁰⁾ has shown that satisfactory deposits of β -alumina can be obtained only with vehicles in a limited range of dielectric constants (12-25). However, Kennedy⁽²²⁾ successfully prepared β -alumina tubes from suspensions using dichloromethane but modified with the addition of trichloroacetic acid.

Even though, benzyl alcohol and amyl alcohol give nearly equal specific yield rates, benzyl alcohol is not preferred as it gives rise to bubbling at higher voltages (> 300 V) because of

TABLE A.III.1

Characteristics of β -alumina Suspensions in Various Vehicles

Vehicle	Viscosity at 15°C millipoise	Dielectric constant*	pH	Conductivity μsec^{-1}	Change in particles	Specific yield rate $\times 10^4$ $\text{g}/\text{cm}^2 \text{ min}^{-1}$
Dichloromethane (B.P. 40°C)		(9.08)	(5.25) 8.25	(0.0274) 0.018	-	negligible
Benzyl alcohol (B.P. 205°C)	(55.82) at 20°C	(13.0)	(5.25) 9.0	(0.926) 20.46	+	4.6
Amyl alcohol-J.P.C. (B.P. 130°C)	(4.811)	(14.7 and 16.0)	(6.0) 8.0	(2.256) 9.09	+	4.25

The numbers in brackets refer to the properties of the vehicle used for making the suspension.

* From reference 28.

TABLE A.III.2

Characteristics of β -alumina Suspensions with Various
Sources of Amyl Alcohol

Source of vehicle	Conductivity $\mu \text{v cm}^{-1}$		Specific yield rate $\text{g/cm}^2 \text{ min V}$ $\times 10^4$	Results
	Vehicle	Suspension		
J.P.C.	2.250	3.97	4.25	Bubbling at 300 V Cracks, dripping
S.L.	0.374	2.88	2.22	Bubbling, cracking
H.P.C.	1.214	14.98	5.43	Highly bubbling even at 100 V. No cracks, dripping
Rec. Chem.	0.495	0.04	5.18	Highly bubbling even at 100 V
B.D.H.				
(a) 5 years old stock	0.887	2.4	1.225	Bubbling at 1000 V No cracks, no dripping
(b) very old stock	1.3048	11.58	3.5	Bubbling even at 100 V. No cracks, dripping
(c) new stock	0.23	1.44	4.42	No bubbling even upto 2300 V. No cracks, no dripping

higher conductivity of the suspension. Also, the liquid entrapped in the deposit is viscous and dries up very slowly (b.p. 205°C) and so deformation of the deposit occurs in the process of drying. From this study, it is clear that amyl alcohol is preferable to other liquids, and hence was used for further experimentation.

Different sources of amyl alcohol viz., J.P.C., S.D., H.P.C., Rec. Chem. and B.D.H. (of 3 different stocks) were evaluated (Table A.III.2) for the electrophoretic deposition of β -alumina on the basis of quality of the deposit (non bubbling of deposit at higher voltages viz., \approx 1000 V). From Table A.III.2, it is clear that, there is no direct correlation between the conductivity of the vehicle and suspension on the specific yield rate. It is because of the fact that the concentration of the suspension was not equal in all the suspensions (varied from 45 to 55 g/100 cc suspension) and the experiments were done in different seasons where the room temperature and humidity varied to a great extent. But, one general observation was that lower the conductivity of the suspension, higher voltages can be applied without bubbling. Lower zeta potential liquids⁽²³⁾ and higher voltages⁽²⁰⁾ were suggested for good electrophoretic deposition of β -alumina. By going for higher voltages, the time required to get a required thickness of deposit decreases and the suspension stability will not be that big a problem. Also, the amount of dripping was less. To go for higher voltages, low conductivity suspension have to be used, otherwise bubbling of the deposit occurs. So, it is preferable to choose a low conductivity vehicle

source. New stock is preferred over old stock as the conductivity of the old stock is substantially high. Amyl alcohol (BDH) new stock was found to be preferable for electrophoretic deposition of β -alumina (Table A.III.2).

A.III.2 Concentration: The effect of concentration of the suspension (g/100 cc suspension) on amount sticking to the mandrel (g/cm^2), conductivity of the suspension and specific yield was studied as follows. 40 g powder in 50 cc amyl alcohol (H.P.C.) was ground in a ball jar for 5 hrs and then the suspension was decanted into the steel can. By adding fresh vehicle to the suspension, the concentration of the suspension was varied. At each concentration, deposition was done at 100 V for 1 minute to find the specific yield. At these concentrations mandrels were dipped upto the bottom of the can and taken out. Then they were dried to find the amount sticking to the mandrel. The concentration of the suspension was computed using the method described in Section A.II.7. The variation of conductivity of the suspension, amount sticking, observed specific yield and actual specific yield with concentration of the suspension is shown in Fig.

A.III.1. The conductivity of the suspension increases non-linearly with decrease of concentration of the suspension. For a concentration variation from 76 to 28 g/100 cc suspension, the conductivity increased from 14 to $24 \times 10^4 \text{ cm}^{-1}$. The amount of solid(suspension) sticking to the mandrel when dipped in it is a function of the viscosity of the suspension. The viscosity of

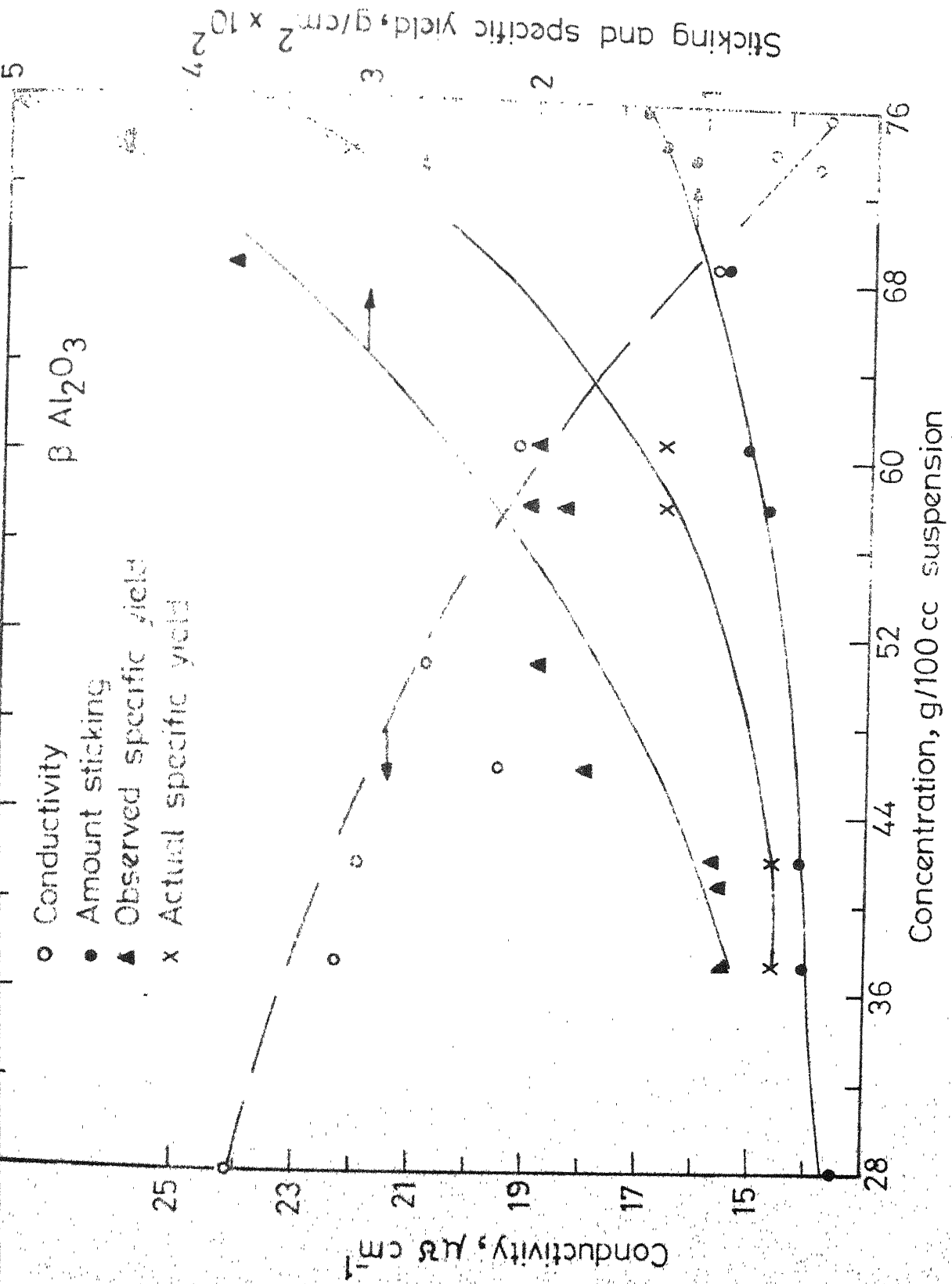


Fig. A III.1. Variation of conductivity of suspension, amount sticking and specific yield with concentration of the suspension.

the suspension increases non-linearly and with a steep increase at higher concentrations (see Section I.4.1). From Fig. A.III.1, it is clear that, the amount sticking to mandrel increases drastically at higher concentrations. Powers⁽²⁰⁾ and Andrews et al⁽²⁵⁾ noticed decreased yield rate as the concentration decreases. In the present study the observed specific yield increases non-linearly with concentration of the suspension. The actual specific yield was computed by subtracting the amount sticking to the mandrel from the observed specific yield. The actual specific yield also increases non-linearly with concentration of the suspension with drastic increment above 60 g/100 cc suspension (Fig. A.III.1). These results may be compared with those of Powers⁽²⁰⁾ on β -alumina and Andrews et al⁽²⁵⁾ on alumina. Starting with a concentration of 50 g in 100 cc of amyl alcohol, Powers⁽²⁰⁾ carried out a number of depositions till 80% of the solids was deposited. The yield rate (g/min) was found to decrease linearly when plotted in terms of the deposit number. With the data available it is, however, not possible to express it in terms of concentration. On the other hand, Andrews et al⁽²⁵⁾ covered a much wider range of concentration. For example, as the concentration decreased from 360 gms Al_2O_3 /400 cc ethanol to 110 gms Al_2O_3 /400 cc ethanol, the deposition rate (g/min) decreased non-linearly from about 0.5 to 0.1 g/min. In another experiment they have measured the deposition rate in terms of the deposit number and obtained a non-linear behaviour. The present results are consistent with those of Andrews et al⁽²⁵⁾.

As per the equations (I.3, I.4 and I.5), the yield should increase linearly with concentration. The non-linear behaviour observed is attributed to the following: (i) the κ of the suspension (see eq. I.3) may be very low at lower concentrations.⁽²⁶⁾ That is, all the particles reaching the electrode may not be depositing, (ii) the probability that the particles moving more rapidly drag slower particles with them and thus raise the specific yield, as suggested by Avgustinik et al.⁽²⁷⁾; this dragging effect may be more pronounced at higher concentrations, and (iii) the very low conductivity of the suspension at higher concentrations (Fig. A.III.1) which increases the yield as per the eq. (I.5).

A.III.3 Grinding: Ball milling of the suspension increases the charge on the particles (Section I.4.3) and increases the electrophoretic yield.⁽²²⁾ 100 gms of powder in 200 cc amyl alcohol (S.D.) was taken. The suspension was subjected to grinding for zero hours, $1\frac{1}{2}$ hours and 7 hours successively. After each grinding operation, 10 depositions were made using the cell shown in Fig. A.III.2a. Each deposition consumed hardly 1 gm. The effect of grinding of the suspension on specific yield and conductivity of the suspension were measured. The electrophoretic specific yield was measured using two parameters, viz., constant voltage, 25 V for different times of deposition and constant time of 1 minute at different voltages from 25 to 500 V. The specific yield was found to vary linearly with fixed time (Fig. A.III.2) and voltage (Fig. A.III.3). These results are in accordance

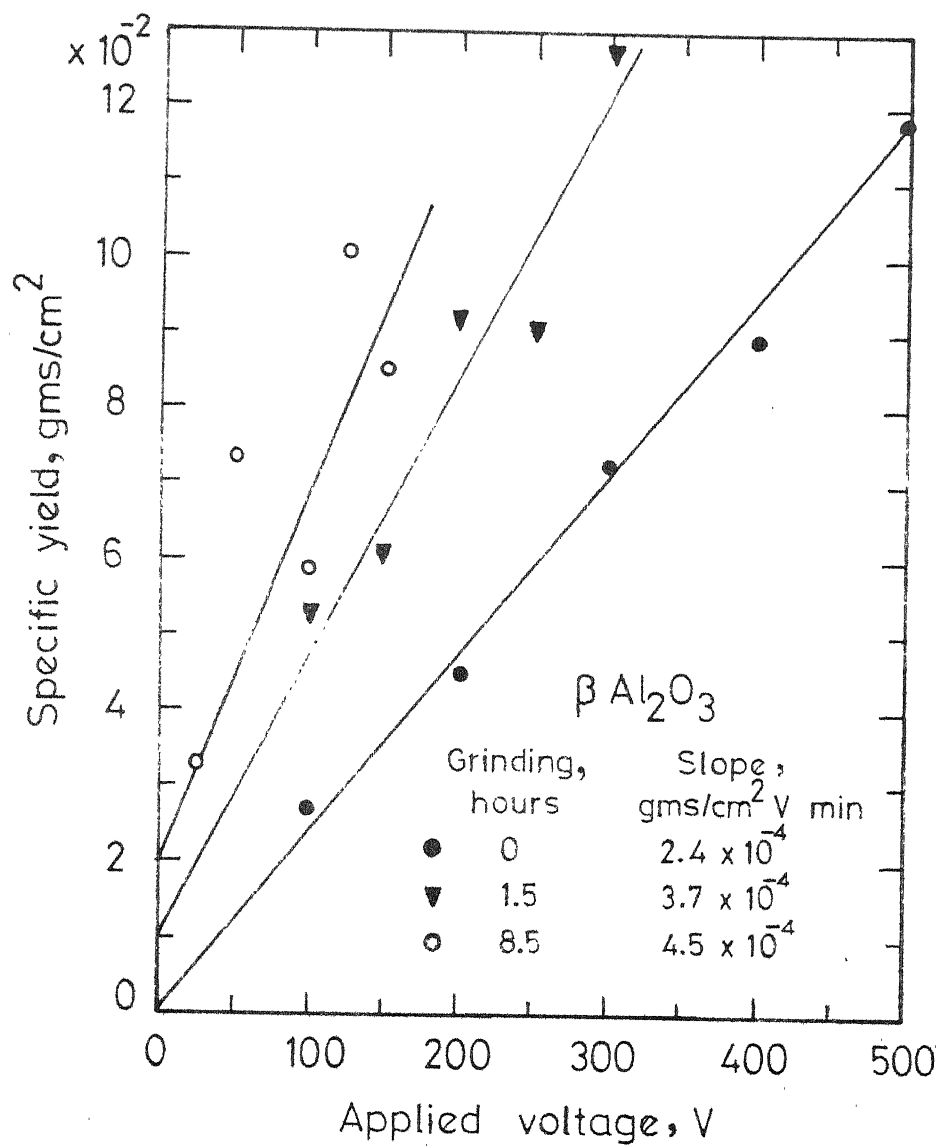


Fig. A III.2. Variation of specific yield with applied voltage (time = 1 min).

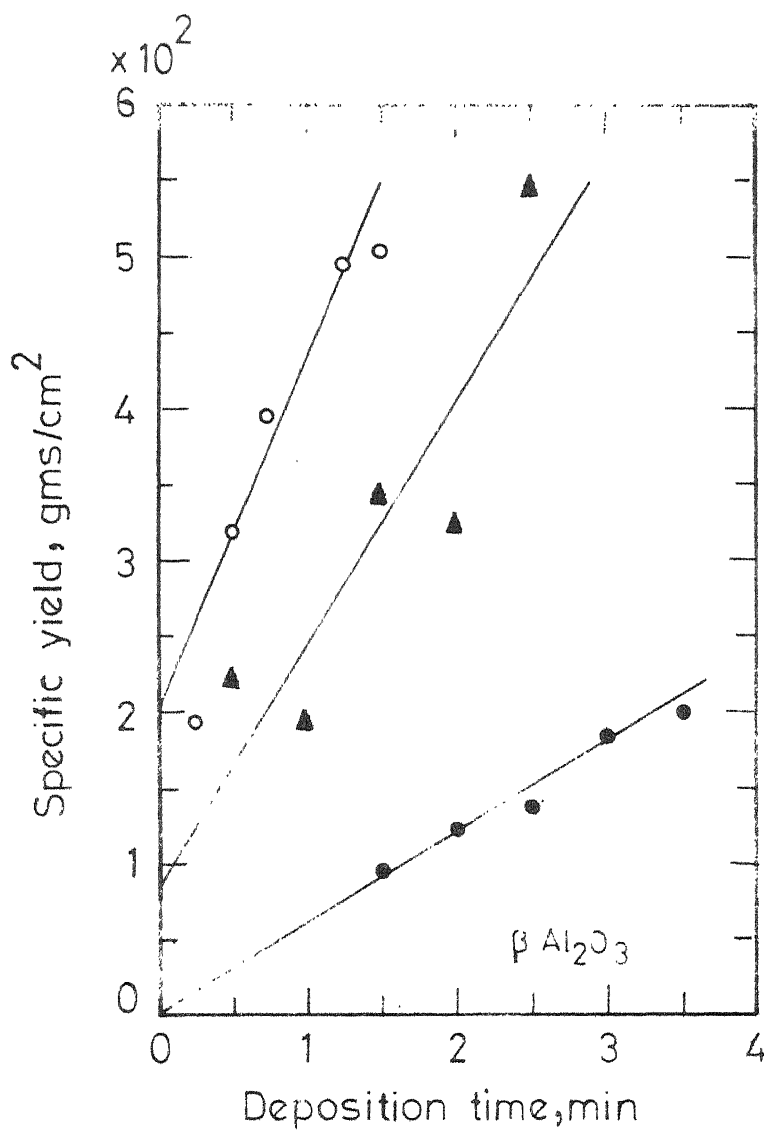


Fig.AIII.3. Variation of specific yield with time (voltage = 25 V).

Grinding, hours	Slope, gms/cm ² V min
● 0	2.4×10^4
▲ 1.5	6.4×10^4
○ 8.5	8.8×10^4

with eqs. (I.3 and I.4) and in agreement with the results of Kennedy and Foissy⁽²²⁾.

Kennedy et al.⁽²²⁾ reported a six fold increase in yield due to grinding for 12 hrs. Grinding of the suspension in a ball mill for 1.5 and 8.5 hrs increased the yield by 2-4 times (Figs. A.III.2 and A.III.3), but the increment in yield was more drastic in the first 1.5 hrs of grinding compared to grinding for 7 more hours. Grinding of the suspension increases the charge on the particles⁽²⁰⁾ and increases the zeta potential⁽²²⁾ which in turn increases the conductivity of the suspension and electrophoretic yield. But, according to eq. (I.5), the yield should decrease with increasing conductivity of the suspension. This statement is true only when the higher conductivity of the suspension is because of extreneous impurities and not when the charge on the particles is increased. Our observation is that with grinding, both the conductivity of the suspension and the specific yield increased but, it is more drastic in the first 1.5 hrs grinding only (Fig. A.III.4).

Attention is drawn to the intercepts on the yield axis in Figs. A.III.2 and A.III.3, which may be due to the sticking of the suspension to the mandrel dipped in it. This sticking increases with the grinding of the suspension possibly because of increased viscosity.^(22,24)

The slopes of the lines in Figs. A.III.2 and A.III.3 give specific yield rates in $\text{g/cm}^2 \text{ min V}$, which are indicated in

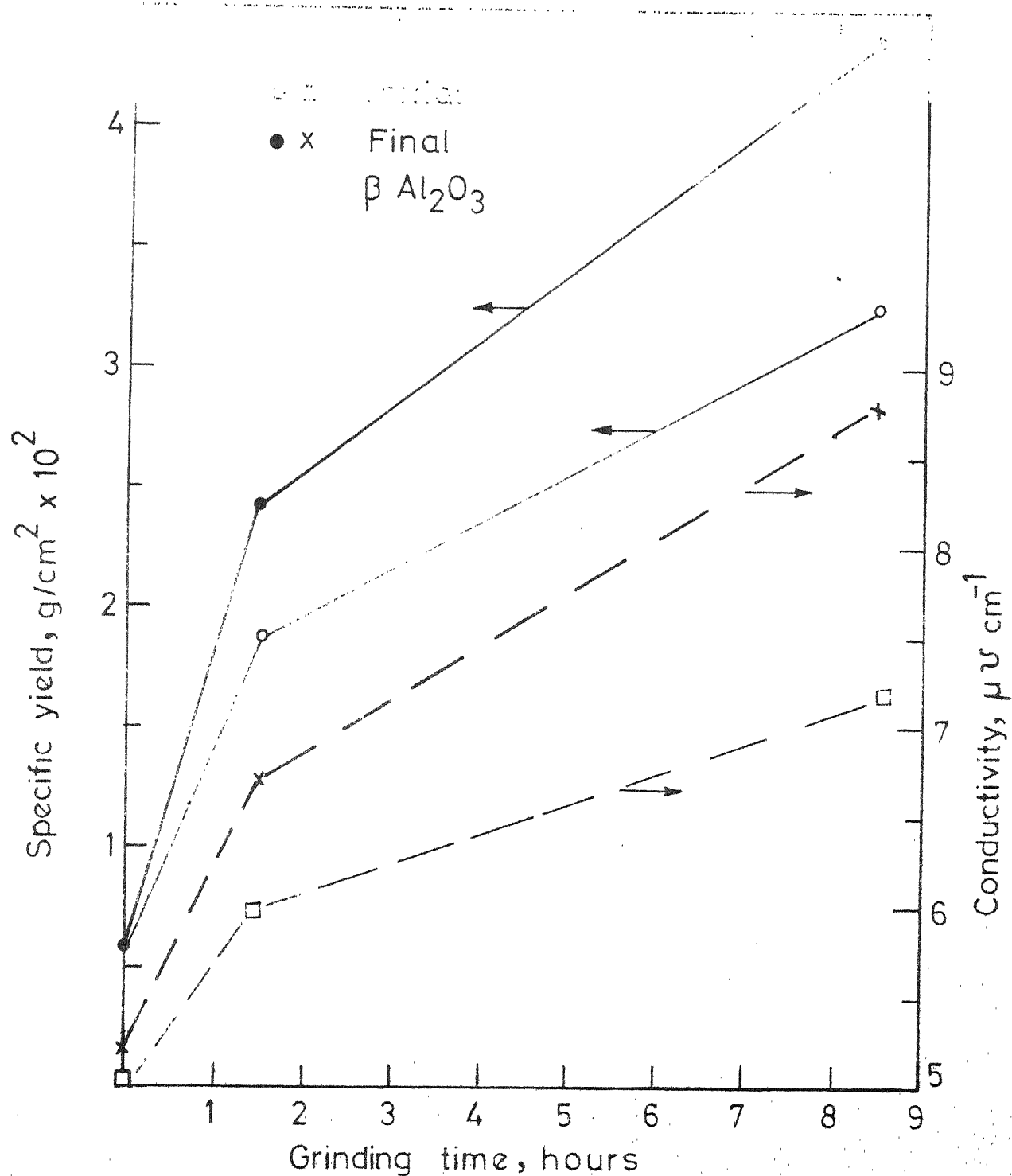


Fig. A III.4. Effect of grinding on conductivity of the suspension and the specific yield at 25 V for 1 min.

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the figures. The specific yield rate values from the two figures are the same for the unground suspension (2.4×10^{-4} g/cm² min V), but they differ somewhat for the ground suspensions. The specific yield values from the time dependence study (Fig. A.III.3) are somewhat higher than those from the voltage dependence data (Fig. A.III.2), which were collected first. This may be due to increase in moisture content which might have increased the charge on the particles because of adsorption mode (Section A.I.2.4) and thereby the conductivity of the suspension (Fig. A.III.4). Fig. A.III.4 shows that the conductivity of the suspension is higher at the end of a set of depositions than at the beginning of the depositions. This increase in conductivity may be due to the decrease in concentration caused by a series of depositions, as suggested by data in Section A.III.2. The deposition yields observed by Kennedy and Foissy⁽²²⁾ who used dichloromethane with an addition of an acid as the vehicle are 2-3 times larger than those obtained here. This may be due to the addition of an acid (see Section A.III.5) and the effect of longer grinding times on the charge of the particles.

A.III.4 Temperature: The effect of temperature on conductivity of the suspension and specific yield was studied as follows. 80 g powder in 150 cc amyl alcohol (BDH) was ground for 5 hrs and then decanted into the steel can. The depositions were done at 100 V for 1 min. After obtaining one deposition at room temperature, the suspension with the can and mandrel were heated

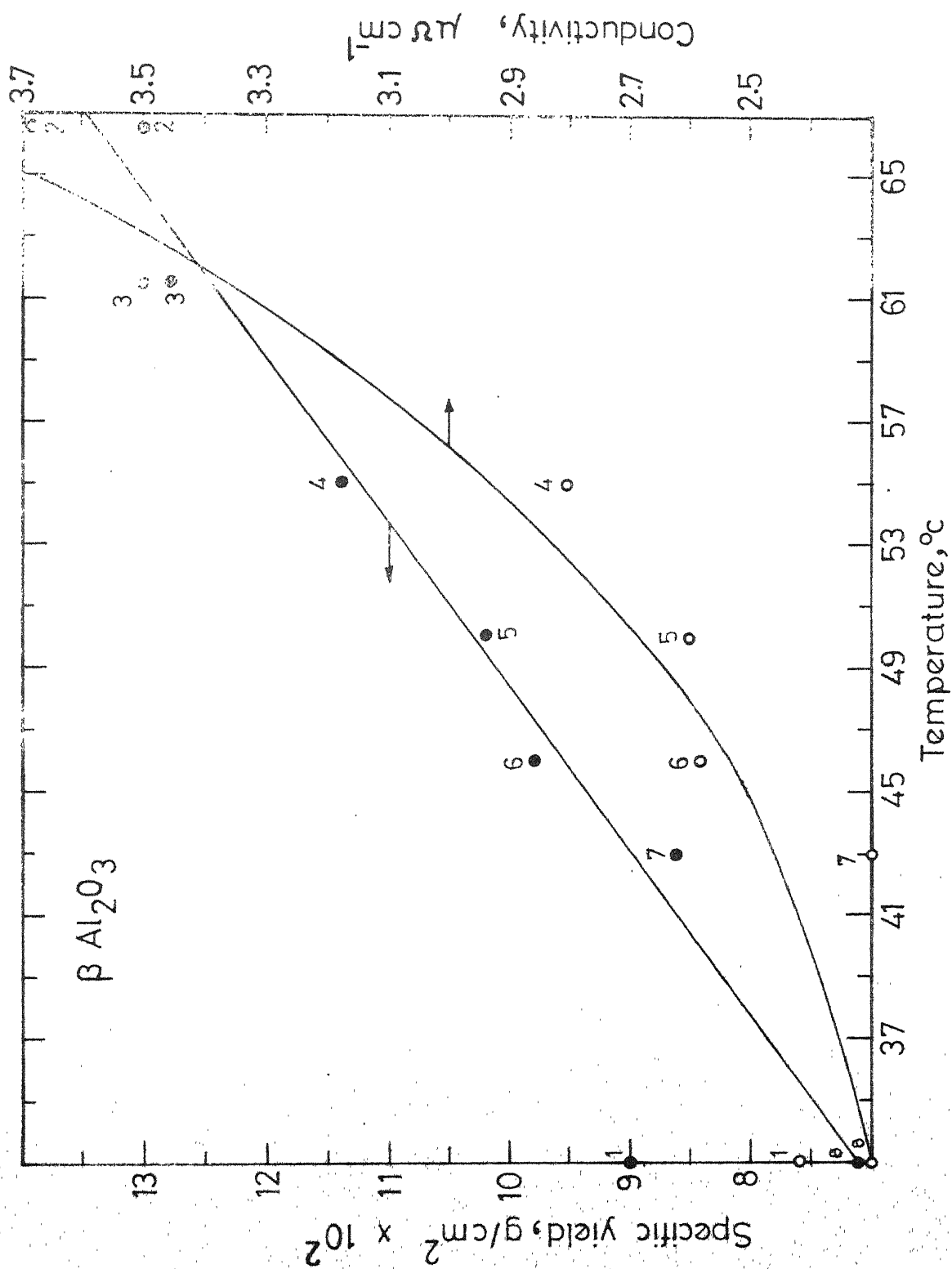


Fig. A III.5. Variation of specific yield and conductivity of the suspension with temperature.

to 70°C in an oven and then taken out. Heating the suspension with the mandrel enhances the heat conduction and the suspension gets heated up more or less uniformly. As the suspension cools down, the depositions were done. The temperature of the suspension was noted and the suspension was stirred for the next deposition. It was observed that, as the temperature of the suspension increases, the specific yield increases linearly (Fig. A.III.5). The sequence of deposition was also included in the figure. The specific yield of first deposit was only 1.27 times that of the eighth deposit as the concentration varied from 45-30 g/100 cc suspension. It may be noted that both these depositions were carried out at room temperature, namely 33°C. Increase in yield with temperature (between -20 and +40°C) of the suspension was also observed by Andrews et al.⁽²⁵⁾ in the case of suspensions of alumina in ethanol.

A.III.5 Additives: (i) Ethyl glycol monoethyl ether: Addition of ≈ 0.5 cc of this additive to 50 cc of the ground suspension increased the specific yield by 8.3 times. The conductivity of the suspension increased by ≈ 2.5 times but there was no bubbling even at 1000 V. The increased conductivity of the suspension may be because of the increased charge on the particles with glycol (proton) adsorption. The specific yield and the conductivity of the suspension varied nearly linearly with the concentration of the suspension (Fig. A.III.6), verifying eqs.

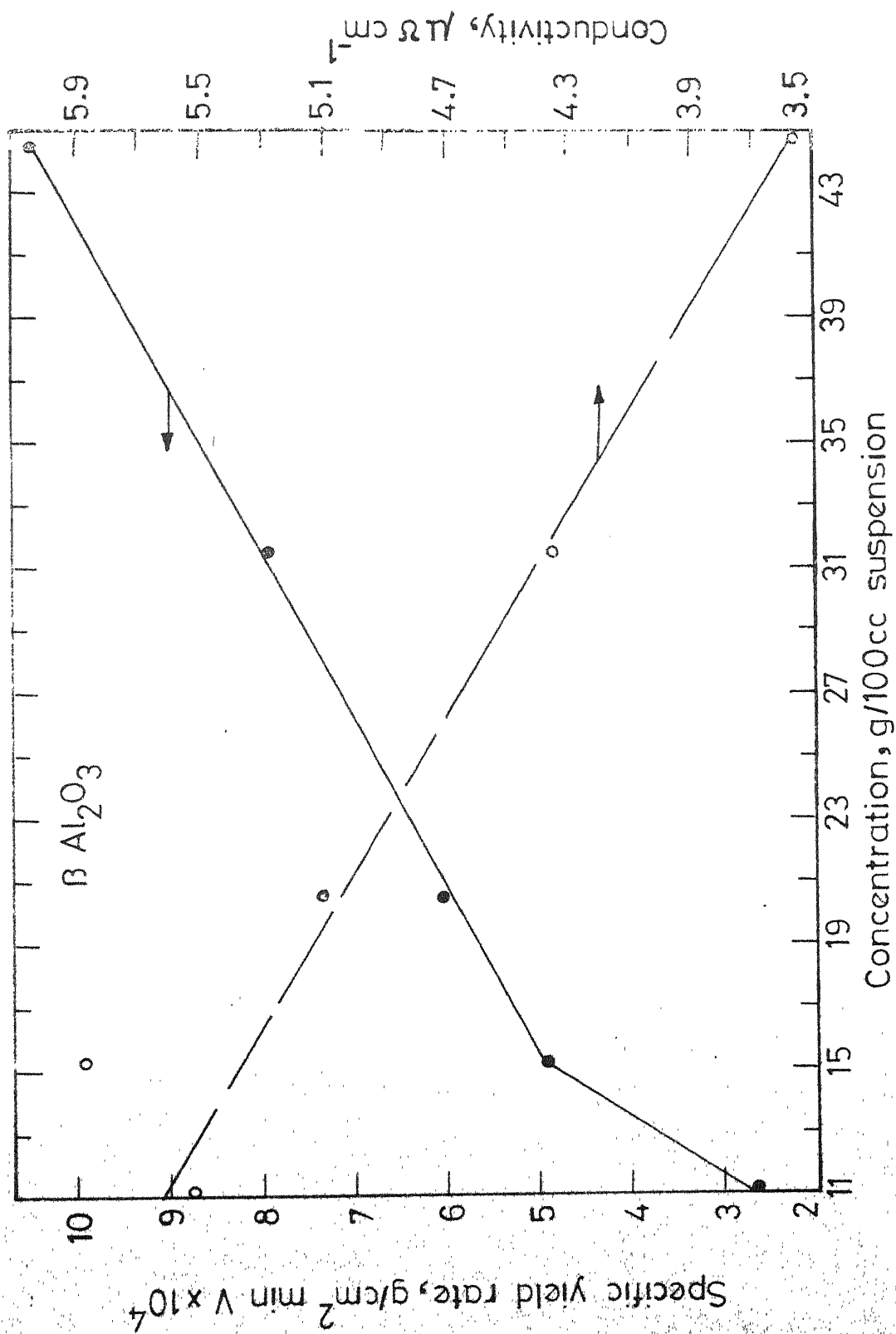


Fig.A III.6. Variation of specific yield and conductivity of the suspension with concentration of the suspension containing ethylene glycol.

(I.3, I.4 and I.5). It was observed that adding the ethylene glycol to the ground suspension gives more specific yield than the addition before grinding and this aspect requires further study.

(ii) Trichloroacetic acid: 3 drops of this acid addition to 30 cc of the suspension increased the specific yield rate marginally and the conductivity of the suspension by 7.7 times that of the suspension with^{out} the addition of the acid. Since the conductivity increased by so much, it is not advisable to use this acid as it leads to bubbling.

A.III.6 Electrode Separation: Electrode separation on specific yield was studied by using (a) a steel can of dia 2.85 cm (Fig. A.II.2b) and a perforated steel tube of dia 4.7 cm (Fig. A.II.2a) as counter electrodes and a steel rod of dia 0.83 cm as coating electrode and (b) steel can of dia 2.85 cm of the counter electrode with steel mandrel (0.83 cm dia) and graphite rods (1.24 and 0.74 cm dia) as the coating electrodes. The specific yield ratios are shown in Table A.III.3.

The subscripts GB, GS, s, p and c refer to the graphite big, graphite small, steel mandrel, perforated steel tube and steel can respectively.

From the Table A.III.3, it is clear that the experimental values, $\frac{\gamma_p}{\gamma_c}$ and $\frac{\gamma_{GS}}{\gamma_s}$ are in good agreement with the values calculated by eq. (I.4). But in the case of γ_{GS}/γ_{GB} and γ_s/γ_{GB} , the experimental values are 1.4 to 2.8 times that of the

TABLE A.III.3

Electrode Separation on Specific Yield Ratios

Ratio	Experimental	Calculated by equation (I.4)	<u>Experimental</u> <u>Calculated</u>
$\frac{\gamma_p}{\gamma_c}$	0.75	0.71	1.05
$\frac{\gamma_{GS}}{\gamma_s}$	0.99	0.92	1.07
$\frac{\gamma_{GS}}{\gamma_{GB}}$	1.3 to 1.9	0.68	1.91 to 2.8
$\frac{\gamma_s}{\gamma_{GB}}$	1.03 to 1.25	0.75	1.37 to 1.67

calculated values by eq. (I.4). This difficulty is arising only when the large dia graphite rod is used for depositions. This may be accounted for as follows: when a graphite rod of dia 1.4 cm is used in conjunction with a steel can of 2.85 cm dia, the amount of liquid between the two electrodes becomes very limited. As the deposition takes place, the concentration of the suspension in that region decreases drastically and the rate of deposition goes on decreasing. So, the specific yield rate on big graphite rod is very less. So, from this study, it is clear that there is a certain minimum for electrode separation for the eq. (I.4) to be valid.

A.IV SUMMARY AND CONCLUSIONS

A number of vehicles (dichloromethane, benzyl alcohol and five different varieties of amyl alcohol) were evaluated for their suitability as suspension medium for electrophoretic deposition of β -alumina of them, amyl alcohol (BDH) was found to give satisfactory results because of its low conductivity and thereby its utility at higher voltages (≈ 1000 V) without bubbling. With concentration of the suspension, the conductivity of the suspension decreases, the sticking to the mandrel increases and the specific yield increases drastically above 60 g/100 cc suspension. By grinding the suspension, the conductivity of the suspension and the specific yield increased. But the increment is more drastic in the first 1-2 hrs of grinding. The specific yield of electrophoretic deposition was found to vary linearly with voltage and duration of applied field, thereby verifying the relevant kinetic equations. With temperature, the specific yield increased linearly with an accompanying increase in conductivity of the suspension. Addition of ethylene glycol monoethyl ether was found to increase yield by 8 times. Avgustinisk's equation (I.4) relating specific yield to the electrode separation was verified. But, a limitation of this equation was detected when the electrode separation becomes very small.

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PART B

B.I. ELECTROPHORETIC DEPOSITION OF MAGNESIA*

B.I.1 INTRODUCTION

Interest in heat resisting ceramic coatings on metals and in methods of forming such coatings has increased in recent years. Hamaker⁽¹⁾ deposited MgO on a very thin wire electrode from a highly concentrated methanol suspension (3.2 g/cc) at voltage of 20-250 volts for 3 seconds obtaining a specific yield rate of 43 g/cm² min V. The currents were 3 to 66 ma and the current was constant during deposition. Avgustinik et al.⁽²⁾ deposited MgO on a thin copper wire from a dilute suspension of 96 percent ethyl alcohol and 1 percent hydrochloric acid. The specific yield rate was 7.5×10^{-3} to 9.4×10^{-4} g/cm² min V, which nearly agrees with the values of 7.5×10^{-3} to 1.1×10^{-3} g/cm² min V, calculated by eq. (I.4).

B.I.1.1 Present study: The present study deals with the electrophoretic deposition of magnesia on a stainless steel mandrel. The aim is to evaluate some vehicles, viz., benzyl alcohol, amyl alcohol (from three sources) and dichloromethane on the basis of electrophoretic yield rate and the uniformity of the deposit. With the selected vehicle (amyl alcohol), yield was studied as a function of concentration and grinding time of the suspension, voltage and time of deposition and electrode separation. The effect of grinding of the suspension on the conductivity was also examined.

* A paper based on this work is accepted for publication in Am. Ceram. Soc. Bull.

B.I.2 EXPERIMENTAL

The cells used for electrophoresis are shown in Fig. A.II.2 and are described in A.II.4. The only difference was that instead of the steel can in Fig. A.II.2b, a brass can of dia 3.35 cm was used.

Magnesia powder of 98.6 percent purity (Baker Co.) with a particle size distribution (Fig. B.I.1) in the range of 0.6 to 1.8 μ (average particle size 1.2 μ) was used. A mixture of 100 g of the oven dried MgO powder and 200 cc of vehicle was used for the determination of specific yield as a function of voltage, time and electrode separation. The specific yield rate was studied as the concentration of the solids was varied from 10 to 50 g (at intervals of 10 g) in 100 cc of the vehicle. The conductance of the suspension was measured just after grinding and after a set of deposition experiments. An impedance bridge (GR 1608) was used to measure conductance at a frequency of 1 KHz. Values of d.c. conductivity, calculated from the current-voltage behaviour of the suspensions studied, are slightly smaller than the measured a.c. conductivity at 1 KHz.

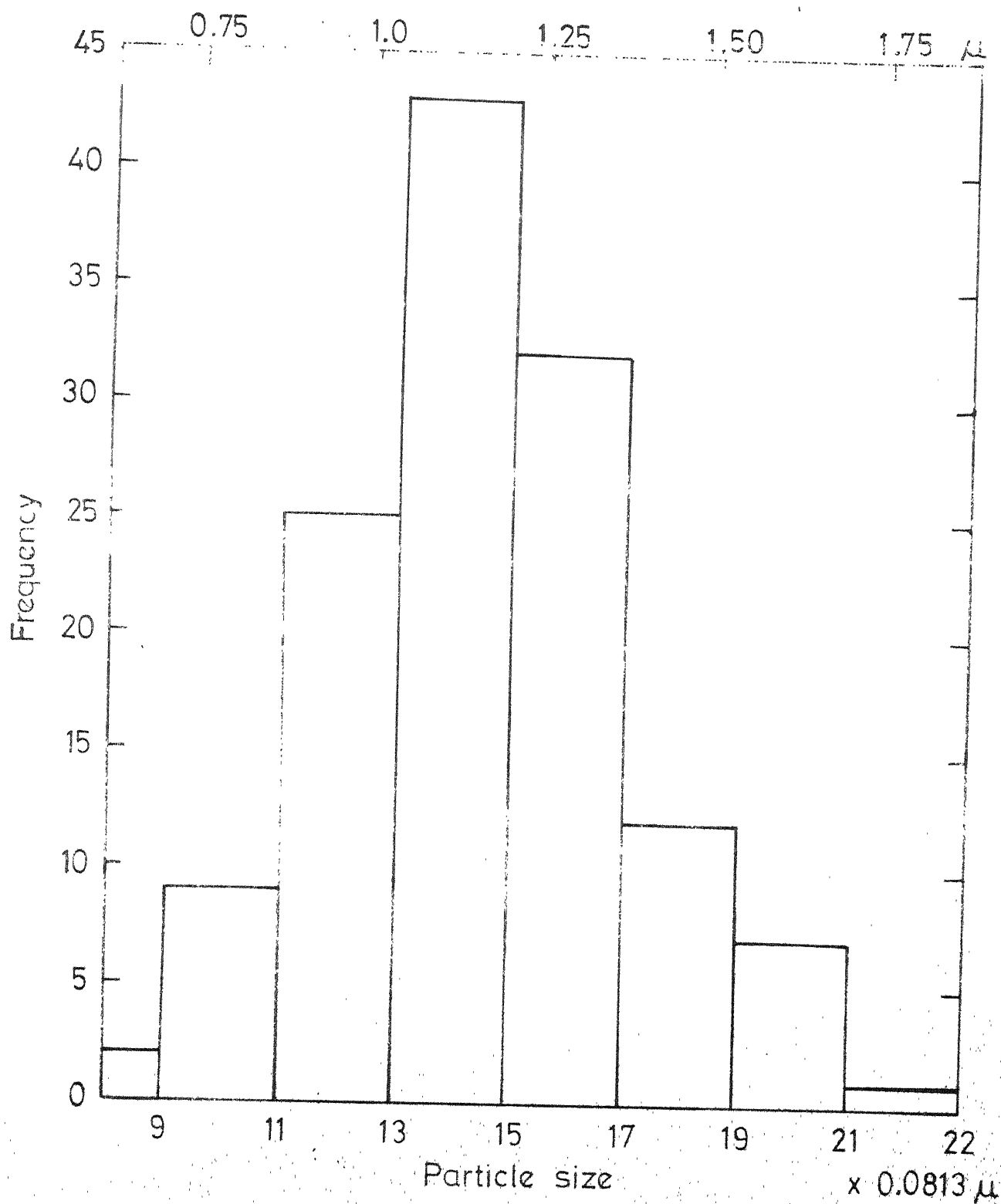


Fig. B1.1. Particle size distribution of MgO
[Baker Co.] powder.

B.I.3 RESULTS AND DISCUSSION

(a) Selection of the vehicle: Dichloromethane, benzyl alcohol and amyl alcohol (from three different sources) were evaluated for the electrophoretic deposition of MgO on the basis of specific yield rate, suspension behaviour and the quality of the deposit (Table B.I.1). The pH of the vehicles was in the range of 5-6 and increased to 8-9 when MgO was added, since MgO is basic in nature (Table B.I.1). On the addition of MgO powder, the conductivity of the liquid increased except for a slight decrease in the case of one brand of amyl alcohol. In all the suspensions, the charge on the particles is positive and the current was less than 5 ma at 200 V. Dichloromethane suspension did not yield any deposit. This may perhaps be due to its low dielectric constant. Powers⁽³⁾ has shown that satisfactory deposits of β -alumina can be obtained only with vehicles in a limited range of dielectric constants (12-25).

Even though benzyl alcohol and amyl alcohols give equal specific yield rates, benzyl alcohol is not preferred because it gives a highly viscous suspension and a fluid deposit, which drips down from the electrode. Also, it dries up very slowly as it has a high boiling point (205°C). From this study, it is clear that amyl alcohol is preferable to other liquids, and hence was used for further experimentation.

TABLE B.I.1

Characteristics of Magnesia Suspensions in Various Media with Concentration of 0.5 g/cc

Suspension	B.P. °C	Viscosity* at 15°C millipoise	pH	Conductivity cm^{-1}	Dielectric* constant	Yield rate $\text{g/cm}^2 \text{ min V}$ $\times 10^4$
Iso-amyl alcohol (J.P.C.)	(130)	(4.811)		(2.256)	(14.7 and 16)	5.59
			9.0	1.881		
Iso-amyl alcohol (B.D.)	(130)	(4.811)	(6.0)	(0.374)	(14.7 and 16)	8.1
			8.0	0.57**		
Iso-amyl alcohol (Rec.-Chem.)	(130)	(4.811)		(0.495)**	(14.7 and 16)	8.35
				2.48**		
Benzyl alcohol	(205)	(55.82) at 20°C	(5.25)	(0.926)**	(13)	
			8.0			
Dichloromethane	(40)		(5.25)	(0.0274)	(9.08)	
			8.5	0.05145		Practically no deposition.

The numbers in brackets refer to the properties of the liquid used for making the suspension.

* From reference 5.

**Conductivity values calculated from the V-I plots. Conductivity in other cases was measured at 1 KHz.

(b) Concentration: The depositions from suspensions with concentrations ranging from 10 to 50 g/100 cc were made at 25 V and 100 V for 1 minute (Fig. B.I.2). Upto 20 g/100 cc, the increment in the specific yield rate is slight, but above 20 g/100 cc the rate of increment is drastic. The curve should be a linear one according to eqs. (I.3, I.4 and I.5). This non-linear behaviour is attributed to the following: (i) the σ of the suspension (see eq. I.3) may be very low at lower concentrations.⁽¹⁾ That is, all the particles reaching the electrode may not be depositing, (ii) the probability that the particles moving more rapidly drag slower particles with them and thus raise the specific yield rate, as suggested by Avgustinik et al.⁽²⁾ this dragging effect may be more pronounced at higher concentrations and (iii) the increase in current at a constant voltage, as indicated by the increase in conductivity which is calculated from the I-V characteristics. It may be noted that over the most of the concentration range, the specific yield rates at 25 V and 100 V are nearly the same within the limits of the precision of the present work, in agreement with eqs. (I.3 and I.4). However, at the highest concentrations studied, the specific yield rate at 100 V is less than that at 25 V. It was observed particularly in the case of these concentrated suspensions, part of the deposit drops into the suspension as the mandrel is removed, the amount dropping being larger for the 100 V deposit than for the 25 V deposit; this point needs further study.

(c) Grinding: A mixture of 100 g of powder in 200 cc of liquid is used for the grinding study. After making 10 depositions (each

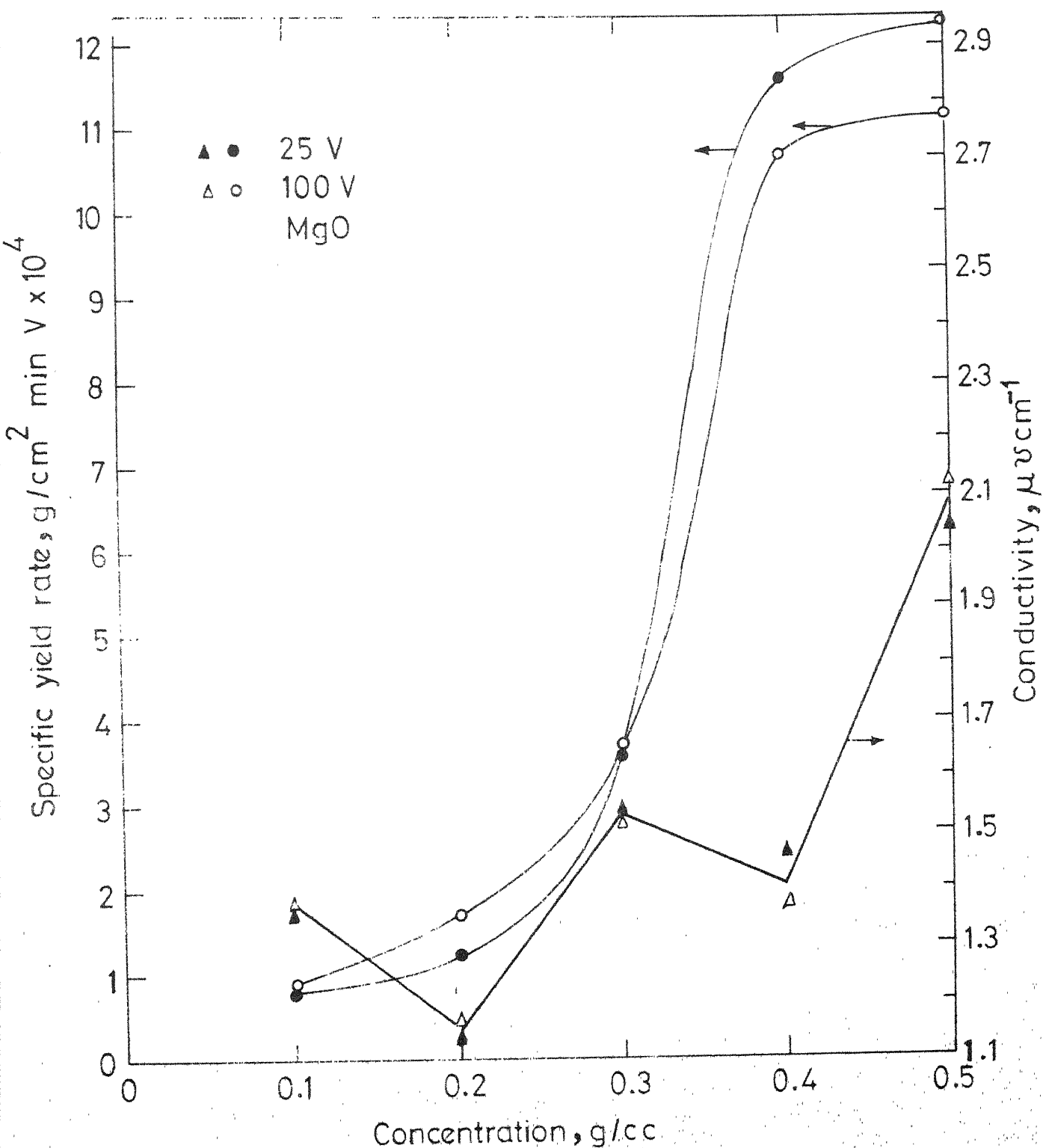


Fig. BI.2. Effect of concentration on conductivity of the suspension and the specific yield at 25 V and 100 V.

deposit weighing ~ 0.5 g), the suspension was ground for 1 hr followed by 10 more depositions and ground for another 7.5 hrs followed by 10 more depositions. The specific yield varies linearly with voltage applied for 1 minute (Fig. E.I.3) and with time at an applied voltage of 25 V (Fig. E.I.4). This is in agreement with eqs. (I.3 and I.4). The slopes of these curves which give the specific yield rate ($\text{g/cm}^2 \text{ min V}$) as shown in the figures do not vary much with grinding. It varied between 7×10^{-4} and $10 \times 10^{-4} \text{ g/cm}^2 \text{ min V}$, which is comparable with that of Avgustinik et al.⁽²⁾ (7.5×10^{-3} to $9.4 \times 10^{-4} \text{ g/cm}^2 \text{ min V}$). Ohm's law is obeyed by these suspensions (Fig. B.I.3). It was also observed that the conductance of the suspension did not change much with grinding in the present case. This may be contrasted with the increased conductance and electrophoretic specific yield rate observed on grinding β -alumina suspensions.⁽⁴⁾

Attention is drawn to the intercepts on the y axis (Figs. B.I.3 and B.I.4), which indicate deposition even before the application of electric field; such sticking of the material to the mandrel must be due to the fine particle size of the powder. This argument is substantiated by the fact that the intercept increases with grinding.

(d) Effect of cell dimensions: Keeping the concentration (50 g/100 cc) of the suspension, deposition parameters (voltage and time) and the inner electrode (mandrel) fixed, depositions were made with two different outer electrodes (Figs. A.II.2a, b). The smaller (3.35 cm dia) electrode, gave a specific yield 1.37 times at 25 V

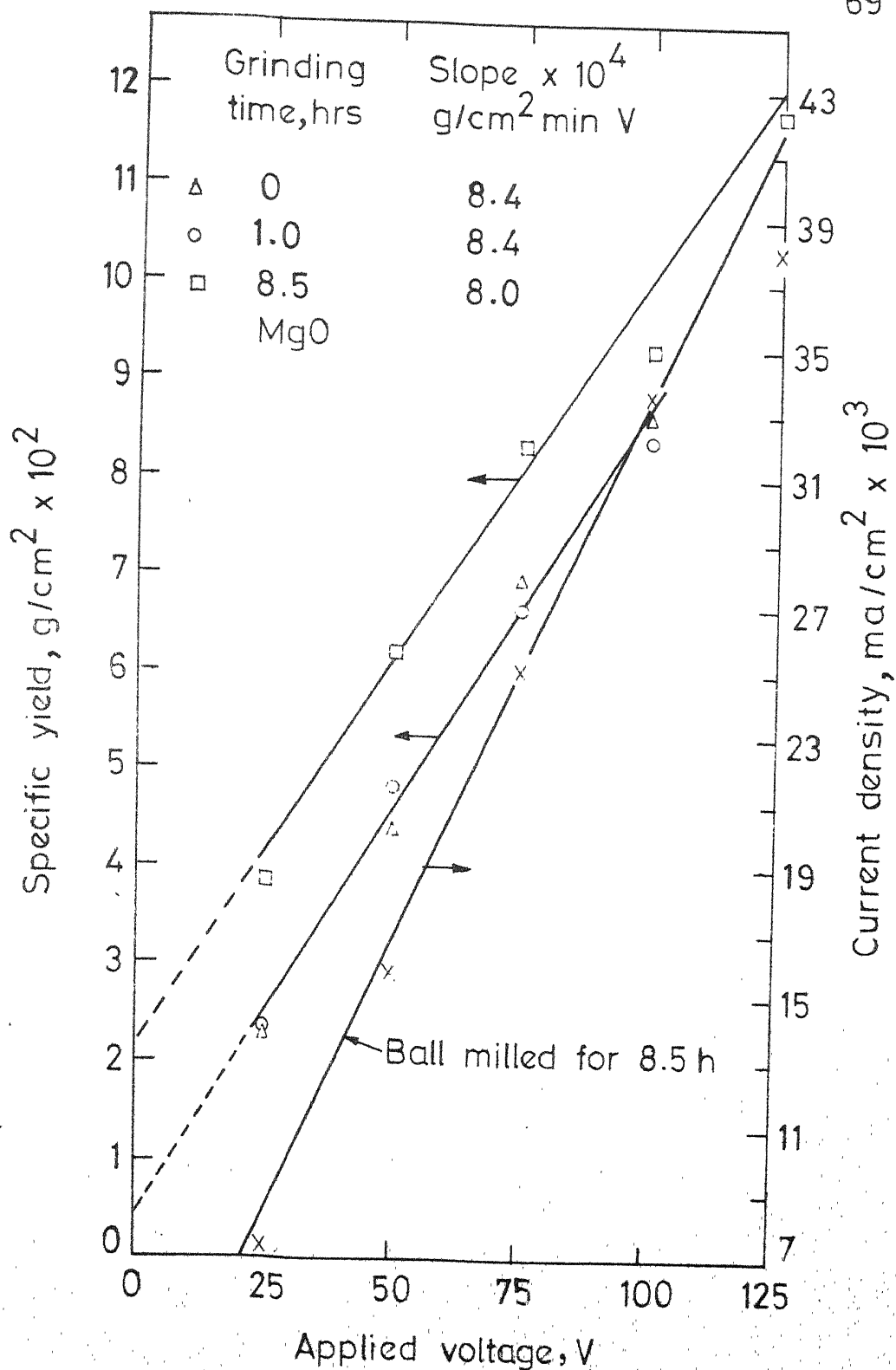


Fig. B I.3. Variation of specific yield (for 1 min) and the current density with applied voltage (suspension ball milled for 0, 1 and 8.5 hrs).

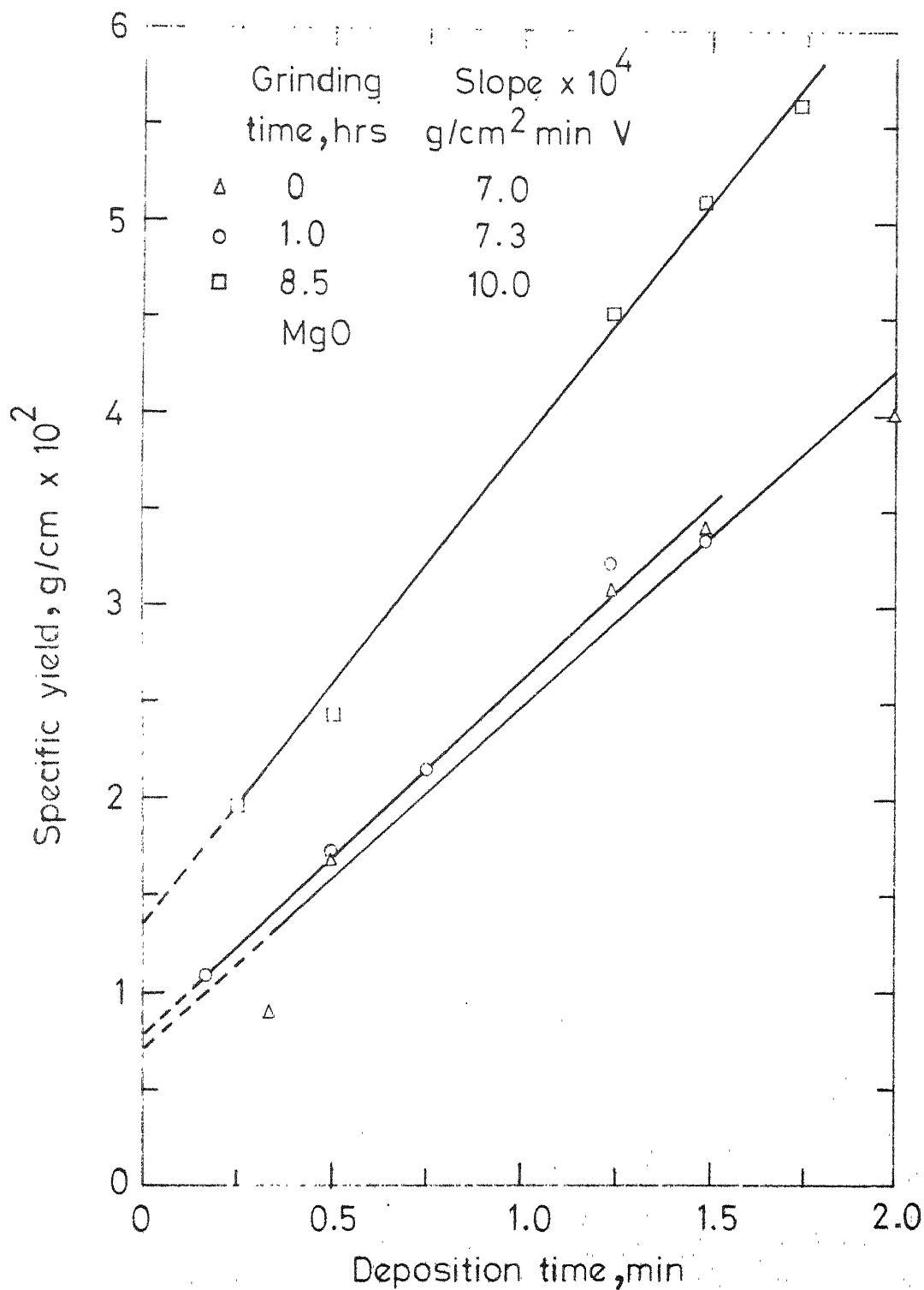


Fig. B.I.4. Variation of specific-yield with deposition time at 25 volts (suspension ball milled for 0, 1 and 8.5 hrs).

and 1.33 times at 100 V larger than that when a larger (4.7 cm dia) electrode was used. This is in reasonable agreement with a ratio of 1.27 calculated from eq. (I.4), assuming that all other conditions were fixed.

(e) Sequence of deposition: Many depositions were made from the same suspension at 25 V for 1 minute. The deposit weight was found to be almost constant, though eqs. (I.3, I.4 and I.5) predict a decrease in yield as the suspension becomes dilute. These data may suggest that with the small amount deposited each time (~ 0.5 g), the concentration of the suspension is not altered sufficiently to affect the specific yield.

B.I.4 SUMMARY AND CONCLUSIONS

Magnesia powder mixed with amyl alcohol provides a suitable suspension for electrophoretic deposition. The specific yield rate is abnormally large for concentrations exceeding 20 g/100 cc. Quantitative relationship between specific yield and applied voltage, time of deposition and electrode separation is verified.

B.II ELECTROPHORETIC DEPOSITION OF ALUMINA

B.II.1 INTRODUCTION

Alumina is a heat, oxidation and corrosion resistant material. Alumina coatings by electrophoresis technique on metallic substrates⁽⁵⁾ and filaments⁽⁶⁾ were already carried out. Andrews et al's⁽⁷⁾ work on electrophoretic forming of alumina bodies is of much interest. Although satisfactory deposits of good strength and cohesion were obtained from several systems, the most suitable suspensions employed a medium of ethanol with dewaxed shellec as a binder for the unfired body. The process has been scaled up to produce ogives 40 cm high with a thickness variation of $\pm 1.5\%$ of a set value. The green densities of the deposits were of the order of 45% of the theoretical density, although an increase upto 53% of the theoretical density was obtained at 40°C. The deposit density was found also to increase with usage of the suspension, and particle-size determinations showed that the increased values were due to preferential deposition of fine particles. The rate of deposition decreased with continued use of suspension as the concentration decreased.

B.II.1.1 Present study: Only a limited amount of study on electrophoretic deposition of alumina was carried out as the results of the preliminary investigations were not very fruitful. The present study deals with evaluating some vehicles viz.,

benzyl alcohol, dichloromethane and iso-amyl alcohol (of two different sources) on the basis of conductivity of the suspension and specific yield rate. Effect of fineness of alumina particles and grinding of the suspension on suspension conductivity and specific yield rate was also tried but with limited success.

B.II.2 EXPERIMENTAL

The cell used for electrophoretic deposition of alumina is shown in Fig. A.II.2a and is described in Section A.II.4. The suspension was prepared by mixing 100 g of alumina powder with 200 cc vehicle. The conductivity of the suspension was computed from the conductance values measured by an impedance bridge (GR 1608). The particle size distribution of alumina powders used were: A-2 alumina 2.5μ to 6.8μ with an average of 4.4μ , Malco alumina fine 3μ to 15μ with an average of 8μ and Malco alumina coarse 4.4μ to 22μ with an average size of 12.2μ . The grinding of the suspension was done by taking 100 g of powder and 200 cc of amyl alcohol (S.D.) in one litre ball jar with 1 Kg cylindrical alumina balls of 1/2" size. The same suspension was used for the successive grindings.

B.II.3 RESULTS AND DISCUSSION

(a) Selection of vehicle: Using A-2 alumina powder, different vehicles viz., dichloromethane, benzyl alcohol and amyl alcohol (S.D.) were evaluated (Table B.II.1). The addition of 100 g of A-2 alumina powder to 200 cc vehicle slightly increased the conductivity of the suspension except in case of dichloromethane. There was no deposition with dichloromethane which has a very low conductivity. The conductivity ratio of benzyl alcohol and amyl alcohol (S.D.) is 1.65 and the specific yield rate ratio of the suspensions with these vehicles is 1.7. Benzyl alcohol suspension has given better yields compared to amyl alcohol (S.D.). The alumina particles were positively charged.

Amyl alcohols of two sources viz., J.P.C. and S.D. were evaluated using 100 g A-2 alumina powder in 200 cc vehicle. The conductivity of J.P.C. vehicle is 6 times that of S.D. amyl alcohol. Instead of the conductivity of the suspension to increase with alumina powder addition, it decreased in case of J.P.C. amyl alcohol. This may be because of very high conductivity of the vehicle which may be impure and no yield was obtained in this case. It was also observed that finer the alumina particles viz., Malco coarse, Malco fine and A-2 alumina added to the vehicle, lower the conductivity of suspension.

TABLE B.II.1

Characteristics of Alumina Suspensions with Different Vehicles

Vehicle	Type of alumina	Conductivity $\mu\Omega \cdot \text{cm}^{-1}$	Specific yield rate, $\times 10^5$ g/cm min V
Dichloromethane	Nil	0.0274	No deposition
	A-2	0.0198	
Benzyl alcohol	Nil	0.926	0.204
	A-2	0.953	
a. Amyl alcohol S.D.	Nil	0.374	0.12
	A-2	0.576	
b. Amyl alcohol J.P.C.	Nil	2.256	No deposition
	Malco coarse	2.036	
	Malco fine	1.818	
	A-2	0.635	

(b) Grinding of the suspension: The suspension was subjected to no grinding, 1 hr and 12 hrs grinding and then the experiments were carried out. As expected from equations (I.4 and I.5), the yield increased linearly with applied voltage and time of deposition. The slopes of these lines with grinding varied from 0.22×10^{-5} to 1.52×10^{-5} g/cm² min V. The conductivity of the suspension was fluctuating with grinding and it varied from 0.3 to 0.7 $\mu\Omega \cdot \text{cm}^{-1}$.

B.II.4 CONCLUSIONS

Among the vehicles studied for electrophoretic deposition of alumina, it was found that benzyl alcohol and amyl alcohol (S.D.) were found to be satisfactory. Vehicles with higher conductivity gave more yield and benzyl alcohol was found to give more yield compared to amyl alcohol (S.D.). For a given type of vehicle, if the conductivity of the vehicle is different for different sources, then lower conductivity vehicle source only gives good yields. This may be because of the impurities in the higher conductivity vehicle. Except in the case of dichloromethane and amyl alcohol (J.P.C.), the addition of alumina powder decreased the conductivity of the suspension. The specific yield increased linearly with applied voltage and time of deposition. Grinding of the suspension on specific yield rate and conductivity of the suspension was fluctuating and grinding of the suspension did not show much effect on yield.

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